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DEVELOPMENT AND EVALUATION OF  
ENVIRONMENTALLY FRIENDLY AND  
PERFORMANCE ENHANCED LUBRICANTS  
FOR MARINE APPLICATIONS

by

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## ABSTRACT

There are many properties of a lubricant which can influence its performance. In order to improve on a lubricant, the application within which the lubricant will be used must be considered to determine which properties are the most crucial. This work has focused on two lubricants, an oil and a grease, which are for use in different marine applications. Improving on the wear performance of both lubricants was a priority in order to improve on the lifetime of these marine systems. Another motivation, particularly for the oil, was to make the new lubricant more environmentally friendly than the currently used mineral oil.

The base fluid for the oil lubricant was chosen to be a polyalkylene glycol based on previous work. The oil would need to be insoluble in water which limited the choice to polypropylene glycols. Additives were evaluated on several bench tests to improve performance properties as needed. The main properties investigated include: wear protection on steel, aluminum, nickel aluminum bronze and manganese bronze systems, foaming tendency and oxidation properties. The current and potential lubricants were examined on a series of bench tests, some of which were developed at the Pennsylvania State University. The proposed replacement fluid is approximately 48 percent biodegradable in comparison to 20 percent for the current mineral oil.

Several commercial greases were compared with a grease currently used in certain marine bearings and gears. The current grease has no extreme pressure (EP) additives and

is unable to adequately protect the bearings from the increasing loads on the system. All the potential replacement greases contained EP additives. The greases were examined for wear, extreme pressure, friction and volatility properties on a series of bench tests. The studies resulted in recommendation of a lithium complex thickened, polyalphaolefin based grease.

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## Chapter 1

### INTRODUCTION

Modern technology is constantly improving at a rapid pace. This is pushing machines to move faster, last longer, and operate at higher temperatures and loads. The more severe demands on machines directly translate to more severe conditions experienced by the lubricants that protect the surfaces in relative motion within the machines. Lubricants must continually be improved to provide the protection required by modern machines. Furthermore, there is growing concern worldwide about the effect of lubricants on the environment. Recent legislation has restricted the use of certain lubricants particularly in several European countries. This research was necessitated by the demand for both increased lubricant performance and increased environmental acceptability from the lubricants. The objective of this research has two specific parts:

- 1) develop an environmentally friendly oil lubricant for use in a marine environment and
- 2) evaluate commercial greases for use in certain marine bearings and gears which will improve the performance and lifetime of the system.

The development of the oil lubricant is to replace an SAE 60 grade mineral oil. The lubricant used in this marine system is periodically discharged into the ocean, but because of the current lubricants poor biodegradability, the discharging of this lubricant is severely restricted. A lubricant which will be less harmful to the environment is required to loosen these restrictions. The system in which the oil is used consists of a large steam

driven engine with two pistons made of aluminum and enclosed in a steel cylinder wall. A titanium rod connects a manganese bronze guide to the pistons. The lubricant is exposed to high temperatures reaching a maximum of 500 °F (260 °C) and the oil is added directly along the cylinder wall at spaced intervals every time the piston goes forward. Excess lubricant becomes mixed in a large water reservoir. A downstream process requires this water-lubricant mixture to flow through a high speed vortex. It is essential that no foam is produced in this vortex. Additionally, any replacement lubricant must provide similar or improved performance characteristics in comparison to the current oil.

Based on previous work on this same application, water insoluble polyalkylene glycols were chosen as a base fluid. Various bench tests were used to evaluate potential base stocks as well as necessary lubricant additives.

In the second system, the evaluation of several commercial greases was required to replace a current grease which was providing an insufficient level of wear protection. This resulted in a shortened lifetime of the bearings in the system. Technological advances had increased the demand on the system in recent years leading to the inadequacy of the current lubricant. These bearings need to withstand severe loads at high speeds for a time period of a few seconds. These loads applications may be as frequently as 1-2 minutes and grease is continually replaced in the system as needed. A secondary concern was the environmental effect of the grease. This concern favored use of a synthetic base oil in the grease over a mineral oil. Bench tests focused on friction and wear testing of the greases in comparison to the current grease. In all respects, the replacement grease should perform better than the current grease.

## Chapter 2

### LITERATURE REVIEW

#### 2.1 Oil Lubricants

Liquid lubricants have been utilized by humans for thousands of years. Initially, crude lubricants as simple as mud on an inclined plane were used. Art from ancient Egypt shows the Egyptians pouring a lubricant in front of a sled that is being pulled [1]. Later, animal and vegetable oils were used to lubricate items of war such as catapults and body armor [2].

Modern liquid lubricants consist primarily of mineral and synthetic oils with the addition of additives where special properties are required. The principal purpose of all lubricants is to minimize friction and wear between two surfaces in relative motion. Other factors of importance include: viscosity, viscosity index, oxidative stability, foam tendency, pour point and corrosion protection.

In addition to the lubricant properties mentioned above, environmental concerns worldwide have resulted in increasing interest in lubricants that are more friendly to the environment. The effect a lubricant has on its environment depends on several lubricant properties including biodegradability, toxicity and the products of biodegradation. Synthetic oils have been the primary lubricant utilized where environmental concerns are considered. Recent studies have examined the possibility of using a vegetable oil based lubricant [3, 4, 5, 6].

### **2.1.1 Biodegradability**

#### **2.1.1 A. Biodegradability Tests**

A lubricant is commonly termed environmentally friendly if it will biodegrade in a reasonable amount of time. Biodegradation is broadly defined as the ability of a chemical substance to be broken down by the metabolic action of living organisms such as bacteria, fungi, yeast and algae. In general, biodegradability can range from a slight transformation, which leaves most of the molecule intact, to complete degradation into carbon dioxide, water and biological matter. Lubricants have commonly been called environmentally acceptable only when the molecule can be broken down enough to remove any biological, chemical or physical property associated with the initial lubricant [7].

At the present time, there is no one test that is agreed upon for measuring biodegradability. Instead, there are a large number of tests with varying conditions. As a result, the biodegradability of a given oil is often different in different tests. Biodegradability is often found to differ significantly from different laboratories running the same test. It is left for the individual's interpretation which test is most representative of the conditions the lubricant will encounter if dispersed in the environment.

Perhaps the most widely recognized test is the CEC-L-33-T82 test developed by the Coordinating European Council for determining the biodegradability of oils in two-stroke outboard engines. Biodegradation is measured as the loss of oil in solvent extracts from inoculated test flasks over that occurring in sterile controls. This is a measure of primary biodegradation. Primary biodegradation is simply the first of sometime many steps in the breaking down of the original lubricant. A lubricant is generally considered

easily biodegradable if it is 70 percent degraded at the end of the test (21 days). This is the only test that can easily be adapted for greases [8].

The Sturm test measures biodegradation by  $\text{CO}_2$  evolution. This is termed ultimate biodegradation meaning the complete conversion of the original lubricant into carbon dioxide, water and biomass. Biodegradation is determined by the ratio of  $\text{CO}_2$  evolved to the theoretical amount of  $\text{CO}_2$  produced for complete degradation. The duration of the Sturm test is 28 days [9]. A third common test is the MITI test which measures the absorption of oxygen. This was set to be a stringent test where fluids typically biodegrade less than in the CEC or Sturm tests. All three tests are all for the assessment of water insoluble products in a water environment.

### **2.1.1 B. Biodegradability of Polyalkylene Glycols**

Polyalkylene glycols as a group are biodegradable. The general tendency is for lower molecular weight molecules to biodegrade faster. The speed and completeness of the biodegradation also varies with the environment and type of bacteria. Polyethylene glycol with a molecular weight of 6,000 has been shown to be 99 percent degraded with certain bacteria [10].

Polyalkylene glycols metabolize from the end of the molecules [11]. First, the hydroxyl group is converted to carboxylic acid. This is followed by ether cleavage. Biodegradation of high molecular weight molecules is slowed by the low concentration of hydroxyl end groups. One technique that has been found to increase the overall speed of biodegradation of polyalkylene glycols is to treat the oil with ozone [12, 13]. The

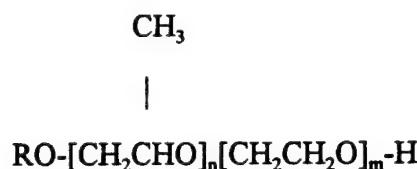
biodegradability of several polyalkylene glycols based on the Sturm test is given in

Table 2.1.

### 2.1.2 Preparation of Polyalkylene Glycols

The production of polyalkylene glycols begins with either ethylene oxide or propylene oxide. An alcohol and a smaller amount of metal alkoxide are used to start the reaction. In the case of propylene oxide, the metal alkoxide reacts with the propylene oxide to form an alkoxide derivative of a new alcohol. This new alcohol is in equilibrium with the other alcohols which allows the next reaction with a propylene oxide molecule to occur either with a molecule that has reacted already or with a new alcohol. With propylene oxide, 96 percent of the reactions form secondary hydroxyl groups leaving only 4 percent as a primary hydroxyl [11]. The reactions with ethylene oxide form identical products regardless of which carbon is the reactive site.

The ethylene oxide and propylene oxide copolymers may be either random or block polymers. The generalized formula for polyalkylene glycols is:



Increasing ethylene oxide to propylene oxide ratios provide greater solubility in water due to the increasing polarity of the molecule. Polyalkylene glycols composed entirely of

Table 2.1 Sturm Biodegradation of Select Polyalkylene Glycols

Average Molecular Weight	Viscosity (cSt)		Viscosity Index	Sturm Test Biodegradation (% biodeg., 28 days)
	100 C	40 C		
<b>Polypropylene Glycols (100% propylene oxide)</b>				
340	2.73	10.9	83	84
640	5.65	26.5	161	84 - 99
740	6.71	32.6	169	99
1020	10.8	56.6	184	85
1550	21.4	124	200	48
2490	51.9	338	219	23
<b>Polyalkylene Glycol (50:50 ethylene oxide:propylene oxide)</b>				
520	4.6	19.1	165	93
790	11.1	52	212	65
1700	25.6	132	230	45
3930	164	1015	281	7
<b>Polyalkylene Glycol (75:25 ethylene oxide:propylene oxide)</b>				
12000	2545	17850	414	8

propylene oxide have very minimal solubility in water. Other general properties of polyalkylene glycols are given in Table 2.2.

## 2.2 Grease Lubricants

The word "grease" is derived from "crass us", the Latin word for fat. Greases date back to the ancient Egyptians around 1400 BC who used a crude grease substance to lubricate the wheels of their chariots. Their grease consisted of both mutton fat and beef fat which was sometimes mixed with lime (calcium hydroxide). The industrial revolution in the 18th and 19th centuries created a dramatic increase in the demand for greases to lubricate the new machinery. As modern technology requires lubricants to handle more and more severe conditions, grease technology has been continually improving to meet these new demands.

A grease is a solid or semi-solid lubricant containing a thickening agent dispersed in a liquid lubricant. The advantage of a grease over a lubricating oil is the ability of a grease to remain in contact with moving surfaces and to not leak out under gravity, pressure or centrifugal action. Greases are chosen over oil lubricants in applications where leakage of the oil would occur, the natural sealing action of a grease is needed or where an increased film thickness is necessary.

The liquid lubricant or base oil commonly accounts for 70 - 95 weight percent of the grease. The base oil may be a mineral, synthetic or natural oil. The thickening agents are between 5 - 25 weight percent. Today, metallic soaps are the most common, particularly lithium soaps which account for over 60 percent of the grease market.

Table 2.2 Physical Properties of Select Polyalkylene Glycols

Average Molecular Weight	Viscosity (cSt)		Viscosity Index	Specific Gravity (20/20 C)	Pour Point (C)	Flash Point (ASTM D92) (C)
	100 C	40 C				
<b>Polypropylene Glycols (100% propylene oxide)</b>						
340	2.73	10.9	83	0.960	-57	152
640	5.65	26.5	161	0.981	-48	221
740	6.71	32.6	169	0.983	-46	265
1020	10.8	56.6	184	0.989	-40	235
1200	14.0	76.4	190	0.994	-37	232
1420	18.4	104	196	0.997	-34	238
1550	21.4	124	200	1.000	-32	232
2080	36.9	227	214	1.002	-29	235
2490	51.9	338	219	1.002	-23	232
<b>Polyalkylene Glycol (50:50 ethylene oxide:propylene oxide)</b>						
520	4.59	19.1	165	1.023	-65	196
970	11.1	52	212	1.035	-40	238
1590	25.6	132	230	1.051	-34	229
3380	117	700	269	1.062	-29	229
3930	164	1015	281	1.063	-29	232
<b>Polyalkylene Glycol (75:25 ethylene oxide:propylene oxide)</b>						
980	19.6	90.9	184	1.097	-15	241
2470	41.5	282	207	1.099	4	271
6950	250	1800	282	1.094	4	266
15000	2545	17850	414	1.092	4	281

Inorganic materials such as silica, expanded graphite [14] or clays may also be used as thickeners. Clay thickeners normally account for only 5-10 weight percent of the grease [15]. Additives are often required to improve certain properties of the grease such as oxidative stability, wear protection or corrosion. These additives consist of 0-10 weight percent of the grease. These grease additives are often the same as those used in oil lubricants. Exceptions are solid additives such as graphite and molybdenum disulfide which are typical extreme pressure additives. Another grease extreme pressure additive that has recently been introduced and shown even more effective in wear protection under severe conditions is phosphate glass [16]. Under light loads, the phosphate glass was found to maintain its original round shape. In effect, the particles would act as little ball bearings. At very high loads, the phosphate glass particles were found to soften and form a thick protective film on the wear surface.

The ability of a grease to reduce friction and wear is the most important property of a grease as was the case with oil lubricants. Other important factors that need to be considered include: type of thickener, hardness or consistency, dropping point, extreme pressure additives, pumpability, volatility and environmental affects.

### **2.2.1 Grease Thickeners**

Soaps that are used in grease production are made by reacting a long chain fatty material with an alkali. The fatty material may be either an animal fat or a vegetable derived acid, commonly 12-hydroxystearic acid. 12-hydroxystearic acid is derived from castor oil and has a hydroxyl group at the 12 position on the carbon chain of the soap

molecule. Lithium hydroxide, calcium hydroxide, aluminum hydroxide and sodium hydroxide are frequently the alkali materials. Sample reactions for the formation of these soaps are shown in Figure 2.1 [17].

Some regular soaps are being replaced as thickeners by complex soaps. A complex soap generally is formed by the cocrystallization of two or more compounds. One component is a long chain fatty acid similar to a regular soap thickener. The other component is a complexing agent which is commonly the metallic salt of a short chain organic acid. Complex soap fibers generally form a soap network in comparison with regular soap fibers which normally are separated. Greases with complex soap thickeners include lithium complex, calcium complex and aluminum complex. The most important property that separates complex greases from their normal soap counterpart is the higher dropping point of the complex greases. This advantage allows for use in a higher temperature range.

The structure of grease thickeners is very important in regards to the properties of the grease. The soaps form microscopic fibers which form a matrix that hold the base fluid. If the pores between the soap structure are too large the grease may not be stable. According to Boner, the rheological properties of lithium-based grease are a result of the different sized fibers of the soap molecules [18]. The most effective shape of thickener molecules is a thin strip. By increasing the surface area to volume ratio of the thickener molecules, the grease structure is strengthened as indicated by the lower penetration number [19]. Wilson showed lithium soap fibers to be long and flat strips [20]. The fiber structure and surface of the fibers tend to vary with different soaps.

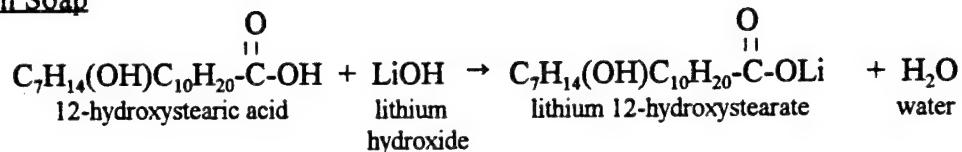
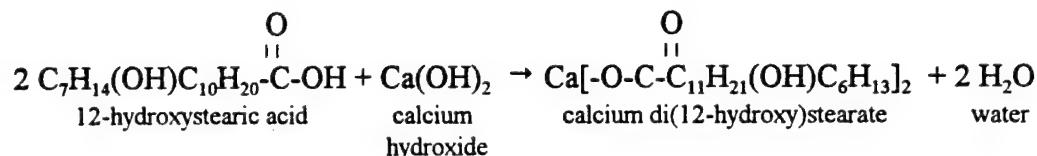
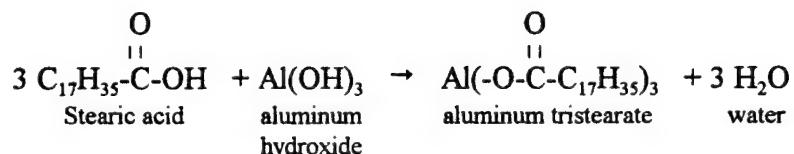
Lithium SoapCalcium SoapAluminum Soap

Figure 2.1 Chemical Reaction for Making Grease Thickeners

The methods a grease will contain the base oil include: intermolecular attraction between the oil and thickener, capillary effects and mechanical retention. Intermolecular attraction may bind up to 25 per cent of the base oil within the grease [21]. The remaining oil is held by capillary effects and mechanical retention.

Different grease thickeners should not be mixed in the same application. Mixing greases may reduce their effectiveness due to excess softening, poor lubrication properties and possibly component damage or failure. Lithium and sodium greases in particular have historically been shown to be incompatible. However, an extensive study by Meade tested over 1200 combinations of greases and found 75 percent of them to be compatible [22].

The type of thickener employed in a grease will also effect stability of the grease after being sheared. Lithium based greases have been shown to have the least reduction in shear stress in a concentric cylinder rheometer and the least reduction in film thickness on a rolling ball on plate test. This provides evidence of stronger structural bonds of lithium greases. It also accounts for a greater activity of broken structural bonds reforming.

Greases that were found to have less structural resistance include calcium, bentonite (clay) and sodium based greases [23].

Each type of thickener has properties that are may prove beneficial or detrimental. General grease characteristics and typical applications are shown in Table 2.3 [17].

Table 2.3 Grease Characteristics and Applications

Thickener Type	Grease Characteristics	Applications
Aluminum	Low dropping point Good water resistance	Low speed bearings Wet applications
Sodium	Poor water resistance Good adhesive properties	Older industrial equipment requiring frequent relubrication
Calcium	Low dropping point Good water resistance	Bearings in wet applications Railroad rail lubricant
Lithium	High dropping point Resistant to softening and leakage Moderate water resistance	Automotive chassis and wheel bearings General industrial grease
Aluminum Complex	Good water resistance Resistant to softening Shorter life at high temperatures	Steel mill roll neck, rolling and plain bearings
Calcium Complex	Good water resistance Inherent EP/load carrying capability	High temperature industrial and automotive bearing applications
Lithium Complex	Resistant to softening and leakage Moderate water resistance	Automotive wheel bearing High temperature industrial service including various roller-element applications
Polyurea	Good water resistance Oxidation resistant Less resistant to softening and leakage	Industrial roller-element bearings Automotive constant velocity joints
Organic-clay	Resistant to leakage Good water resistance	High temperature bearing with frequent relubrication Steel mill roll neck and roll neck bearings

### 2.2.2 Production of Greases

All soap thickened grease manufacturing processes consist of three basic steps: 1) forming the soap, 2) dehydrating and conditioning the soap, 3) dispersing the base oil and additives in the soap. Sometimes an additional step is needed to further disperse the soap. This is done by milling which consists of passing the grease through a shearing device. This shearing action orients the fibers as shown by Brown et al. [24]. The increased dispersion and orientation hardens the greases sometimes as much as 100 penetration units or more as measured by ASTM test method D-217 [25].

There are three main processes by which greases are produced. They are the kettle process, the contactor process and the continuous process. The kettle process is a batch process which takes between 16 to over 24 hours for one batch of grease. The capacity of the kettle generally ranges between 10,000 and 50,000 pounds. The contactor process is very similar to the kettle process with the exception that the production takes place in a pressurized reactor. The advantage of the contactor process are reduced heating and reaction time. For example, a typical 20,000 pound batch of lithium grease may take 20 hours in a kettle process, but only 5-7 hours in a contactor process [17, 26].

The continuous process contains three main sections: the reactor, a dehydration section, and a finishing section. The soap resides in the reactor about 1-5 minutes. The dehydration section operates under a vacuum and is generally heated to 370 °F. Typical residence times are 15 minutes. In the finishing section additional oil and additives are combined and dispersed. The residence time in this section is usually less than one minute [27]. A comparison of the continuous and kettle processes is shown in Table 2.4 [17].

Table 2.4 Comparison of Continuous and Kettle Grease Processing\*

	<u>Continuous Process</u>	<u>Kettle Process</u>
Investment cost factor:	1.0	1.2
Manufacturing cost factor:	1.0	4.1
Heating load, Btu/hr:	1,500,000	3,000,000
Cooling water, gal/min:	75	200
Electrical, kW/hr:	120	380

\* Basis: Plant for manufacturing 10 million lb/yr of lithium, calcium and sodium soap greases

### **2.2.3 Grease Properties**

#### **2.2.3 A. Penetration**

The penetration number of a grease is directly related to the hardness or consistency of the grease. As described in ASTM test method D-217 [25], it is measured by the distance a standard cone will penetrate a grease sample when a standard force is applied. Therefore, a harder grease has a lower penetration number than a softer grease. The National Lubricating Grease Institute (NLGI) has a classification system to rank grease hardness based on this test. The values are based on a “worked penetration” number which means the grease is “worked” for 60 strokes in a standard manner before measuring its penetration. The NLGI classification system is shown in Table 2.5.

#### **2.2.3 B. Dropping Point**

At high temperatures, greases will lose their structure and essentially become a liquid lubricant. The dropping point is determined using a standardized test as described in ASTM test method D-2265 [28]. Essentially a sample is placed in a test cup with a small orifice and heated at a constant rate. The temperature when the first drop of fluid leaves the test cup is defined as the dropping point. The type of thickener is an important factor in the dropping point. The maximum usable temperature of the grease is somewhere below the dropping point of a given grease. Some general guidelines of various thickeners are shown in Table 2.6 [29, 30].

**Table 2.5 NLGI Classification System for Penetration of Greases**

<b>NLGI Grade</b>	<b>Worked Penetration</b>
000	445-475
00	400-430
0	355-385
1	310-340
2	265-295
3	220-250
4	175-205
5	130-160
6	85-115

Table 2.6 General Temperature Properties of Various Thickened Greases

Thickener	Dropping Point (°F)	Max Service Temperature (°F)
Sodium Soap	340-350	250
Calcium Soap	270-290	250
Lithium Soap	390	325
Aluminum Soap	230	175
Calcium Complex	450-500+	350
Lithium Complex	450-500+	350
Aluminum Complex	450-500+	325
Polyurea (non-soap)	500	350
Organo-Clay	> 500	350

## 2.3 General Lubrication

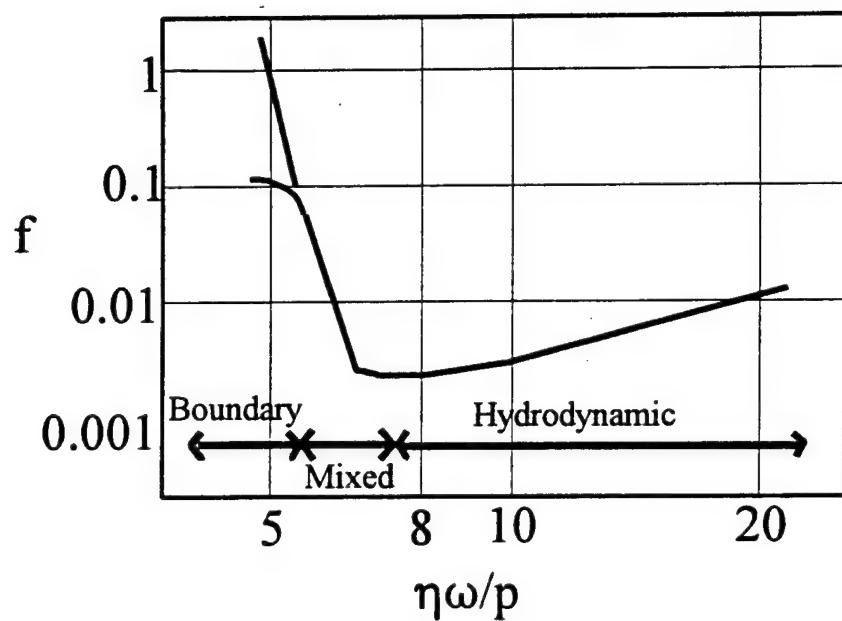
### 2.3.1 Wear

Wear is the result of two surfaces in relative motion and generally results in material loss. Friction is an inevitable companion of wear. By applying a lubricant between the surfaces, the friction and wear can be minimized. Depending on the amount of lubricant film separating the surfaces, the system will fall into one of three lubrication regimes: boundary, elasto-hydrodynamic (also termed mixed) or hydrodynamic lubrication. These three regimes are shown on a Stribeck curve displayed in Figure 2.2 [1]. The Stribeck curve is for journal bearings. Table 2.7 gives approximate thicknesses of the films in each regime as well as the size of other important factors for the boundary regime [31].

Hydrodynamic lubrication is characterized by almost complete separation of the surfaces. The motion and geometry of the surfaces combined with the viscosity of the oil can produce a fluid pressure high enough to completely separate the surfaces.

Elasto-hydrodynamic lubrication occurs when the film thickness is not thick enough to completely separate the surfaces. Incomplete separation results in the surface asperities contacting which leads to the deformation and wear of the asperities. The lubricant in the contact area is continually being replenished at the front of the contact [32]. Despite the occasional contact between asperities, the film thickness in the elasto-hydrodynamic regime is still larger than in boundary lubrication.

Boundary lubrication is defined as the lubrication regime where friction and wear between surfaces in relative motion is determined by both properties of the surfaces and



**Nomenclature:**

- $f$ : friction coefficient
- $\eta$ : lubricant viscosity
- $\omega$ : rate of rotation
- $p$ : nominal bearing pressure

Figure 2.2 The Stribeck Diagram for a Journal Bearing

**Table 2.7** Size Scales Pertinent to Boundary Lubrication

<b>Approximate Size Range (<math>\mu\text{m}</math>)</b>	
Monomolecular layer	0.002-0.2
Sliding wear debris	0.002-0.1
Boundary film	0.002-3
Elastohydrodynamic film	0.01-5
Asperity height	0.01-5
Rolling wear debris	0.07-10
Hydrodynamic film	2-100
Asperity tip radius	10-1000
Concentrated contact width	30-500

properties of the lubricant other than its viscosity. In this regime, the film thickness between the surfaces is on the order of a few molecules thick. Boundary films form on surfaces because they reduce the surface energy and therefore are thermodynamically favored [33]. The film is retained in the contact area by either physical or chemical adsorption.

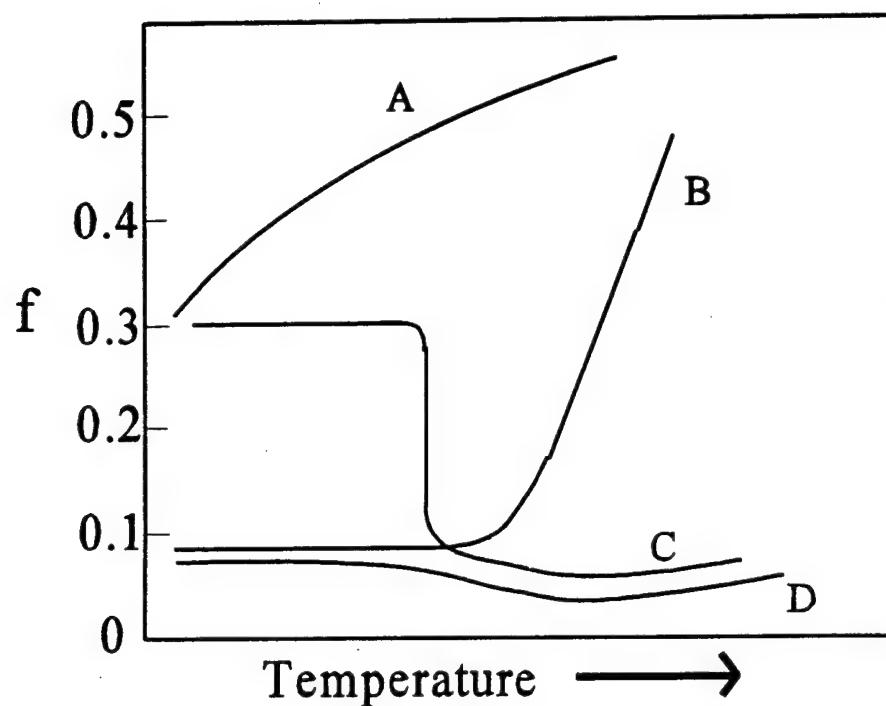
Physical adsorption is a reversible process where molecules orient themselves on the surfaces and provide separation between the two surfaces. Commonly, it is the additives in the lubricant which provide the protection. The additives are typically long chain molecules with an active end group such as alcohols, amines, or fatty acids. Ideally, the molecules pack in tightly and are all oriented with regards to the surface. The close packing helps provide a lateral cohesive force which helps to strengthen the film. As the molecules are pushed away by surface asperities, new molecules from the lubricant will replace them. The simple removal of the boundary molecules leaves the surface unaltered. Physically adsorbed films are effective at low to moderate temperatures.

Chemical adsorption is an irreversible process where a lubricant reacts with the surface forming a protective layer. It is normally an additive in the lubricant which is reacting. The new surface is usually a low shear strength material and is worn preferentially to the original surface. As the new surface is worn away, additional additive reacts forming a new protective layer. Higher temperatures tend to increase the protection from chemical adsorption resulting from a faster reaction rate. Extreme pressure (high temperature) additives rely on chemical adsorption to protect surfaces at temperatures as high as 400 °C. Organic compounds containing sulfur, chlorine or

phosphorus are common extreme pressure additives. They are generally inert at lower temperatures, but at higher temperatures they react with metallic surfaces to form metal sulfides, chlorides or phosphides.

By combining a normal temperature additive with an EP additive, it is possible to provide wear protection and friction reduction over a wide temperature range. An idealized view of this is shown in Figure 2.3. In reality, there is often a gap between the low temperature, physically adsorbed layer and the high temperature, chemical layer. Evidence of this transition is shown by Fuller [34] in Figure 2.4. In this example, oleic acid is the normal wear additive and a chlorinated additive provides the extreme pressure (extreme temperature) protection. The gap occurs around 180 °C indicated by the "bump" in the friction plot.

The semi-solid state of greases which prevents their flow is both an advantage and disadvantage. The advantage is in the ability to remain in systems where an oil lubricant would leak out. The disadvantage is that once grease is removed from the contact point only a minimal amount will replenish what has left. The high yield stress and poor flow properties of greases, make replenishment of the grease in contact areas very slow even under moderate conditions. This often leaves to starvation of the lubricant. In a study by Astrom et al., it was found that greases in fact do show some minimal replacement in the contact area in a similar manner to oils [35]. The replacement was determined by comparing film thickness with replacement to the theoretical predictions of film thickness without replenishment [36].



- A: paraffin oil
- B: fatty acid in lubricant
- C: extreme pressure lubricant
- D: fatty acid + EP lubricant

Figure 2.3 Idealized Frictional Behavior of Lubricants

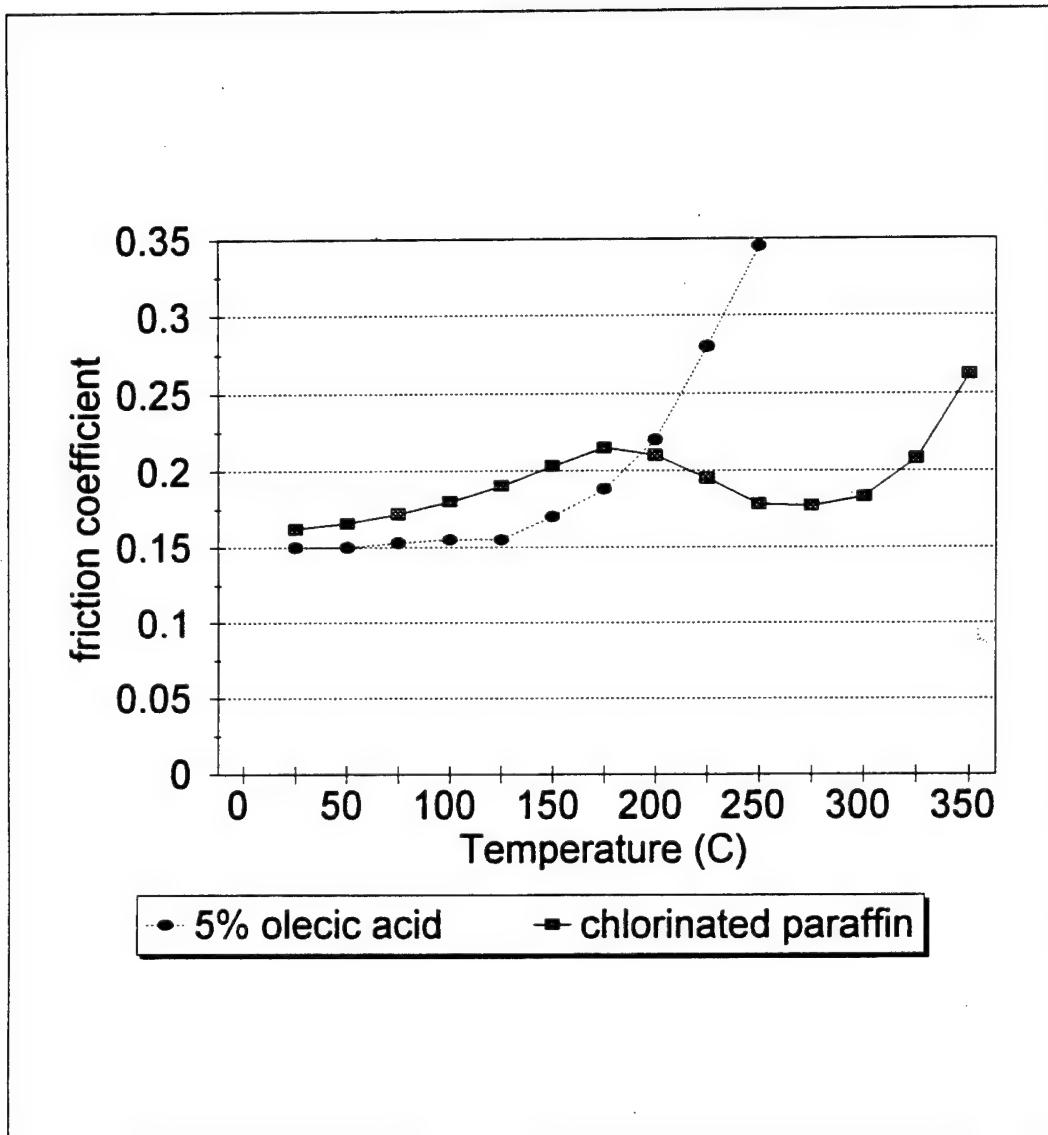


Figure 2.4 Comparison of Paraffin Oil Containing Oleic Acid and EP Additive

### 2.3.2 Friction

Friction is the force opposing the motion of two surfaces in contact with one another in a direction parallel to the surfaces. Large amounts of wear between two surfaces is inevitably joined by high values of friction. By reducing the friction between the two surfaces, the surfaces lifetime can be extended significantly. Reduced friction also translates into energy savings since a smaller force would be required to move a given object at the same rate.

The force of friction between two surfaces is dependent on the magnitude of the normal forces acting on the surfaces. The ratio of the friction force to the normal force is the friction coefficient. The friction coefficient can be simply defined as:

$$f = \frac{F}{W} \quad (1)$$

where  $f$  is the coefficient of friction,  $F$  is the tangential force needed to maintain relative motion and  $W$  is the load. For a hydrodynamic bearing, the coefficient of friction is found to be [1]:

$$f = C * \sqrt{\frac{LU\eta}{W}} \quad (2)$$

where  $C$  is a numerical constant dependent on geometry,  $L$  is the width of the bearing,  $U$  is the relative sliding speed of the surfaces and  $\eta$  is the fluid viscosity.

The two major types of friction are static and kinetic friction. Static friction is the friction between two bodies at rest relative to one another. Static friction prevents relative movement between the two bodies until the applied force is greater than the maximum static friction force between the objects. The friction of objects in relative motion is called kinetic friction. Kinetic friction is generally less than static friction.

In a boundary lubrication environment, the coefficient of friction was derived by Rabinowicz [37]. The force  $F$  needed to shear the contact area is the sum of the force in the area where the film has been removed plus the force in the area where the film remains as shown below:

$$F = \alpha A_r s_m + (1 - \alpha) A_r s_f \quad (3)$$

where  $A_r$  is the area of real contact,  $s_m$  is the shearing strength of metal-to-metal juncture,  $s_f$  is the shearing strength of the boundary film and  $\alpha$  is the fraction of boundary film area which has failed and metal-to-metal contact exists. The load can be shown to equal [38]:

$$W = p_m A_r \quad (4)$$

where  $p_m$  is the hardness of the contacting materials. The coefficient of friction can then be derived:

$$f = \frac{F}{W} = \alpha \frac{s_m}{p_m} + (1 - \alpha) \frac{s_f}{p_m} \quad (5)$$



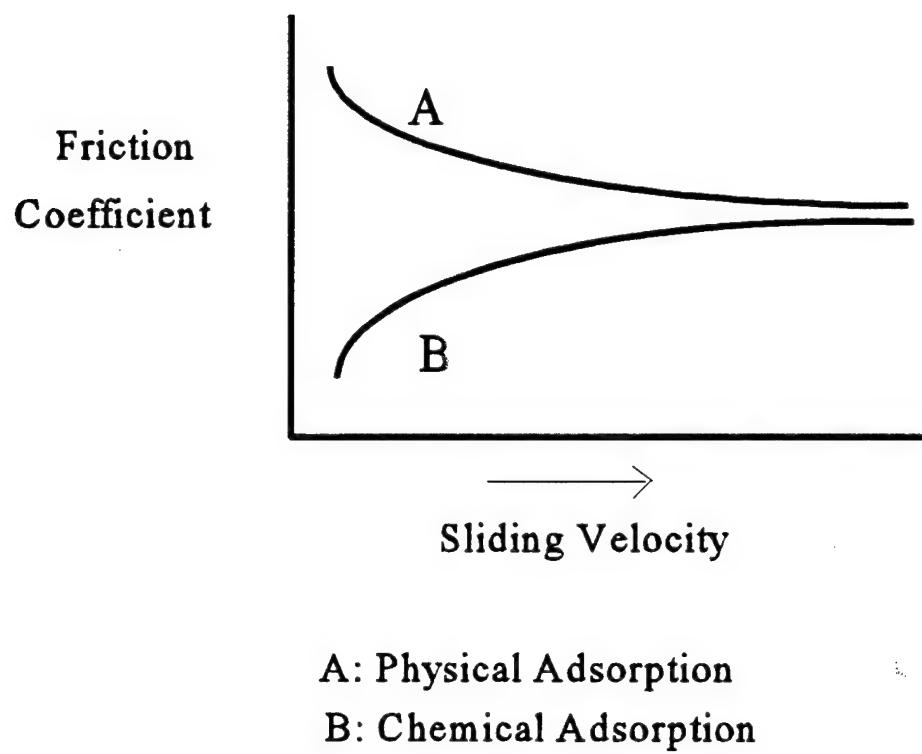
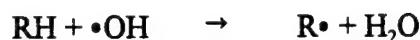
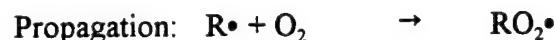


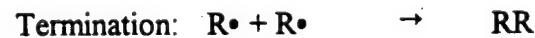
Figure 2.5 Friction Coefficient Versus Velocity

### 2.3.3 Oxidative Stability

Lubricants that are exposed to elevated temperatures are at risk of thermal and oxidative decomposition. The main process by which lubricants degrade is through oxidation. The oxidative degradation of hydrocarbon lubricants and the mechanism by which it occurs has been the focus of extensive research. Hydrocarbons are generally agreed to oxidize in the series of elementary steps shown below [41, 42]:

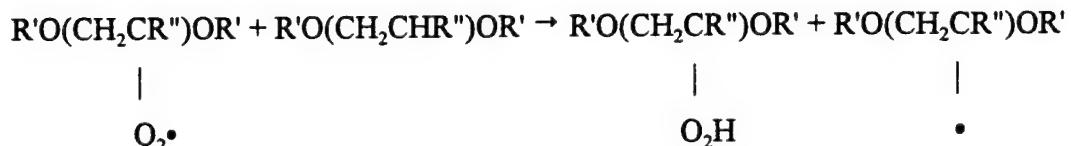


OR



where RH represents a hydrocarbon, ROOH a hydroperoxide, R $\cdot$ , RO $\cdot$ , ROO $\cdot$  the alkyl, alkoxy and peroxy radicals resulting from the hydrocarbon, respectively.

Polyalkylene glycols (PAG) are oxidized by a similar mechanism. The ether oxygen atom that separates every two carbon atoms is the site vulnerable to oxidation. The initiation step leads to the formation of a PAG free radical. The free radical then attacks a carbon adjacent to the ether oxygen within the polymer backbone. The result is a carbon based radical which is stabilized by the adjacent oxygen [11]. This radical is then able to react with oxygen to form a peroxy radical. The peroxy radical can then remove a hydrogen from another PAG to form a hydroperoxide group and regenerate another PAG radical. The chain process can be represented in the series of steps shown below:



Where R' and R" refer to PAG units. Continued decomposition of the hydroperoxide groups form esters, aldehydes and ketones, often by chain cleavage. Further oxidation of the carbonyls leads to the formation of organic acids. All the products that are formed are polar and therefore the polyalkylene glycols, being polar themselves will dissolve the oxidation products. In comparison, when polar products are formed in a mineral oil, the products are insoluble. The polar products will polymerize into higher molecular weight species and form insoluble varnish or sludge.

As the oxidation of the polyalkylene glycol becomes more severe, the oxidation products exist as polymers and degraded lower molecular weight species. The decreased molecular weight of some of the products increases their volatility leading to high evaporation rates with few deposits. This process consisting of high evaporation and low deposit formation is referred to as "clean burnoff" and is characteristic of polyalkylene glycols at high temperatures.

## Chapter 3

### EXPERIMENTAL PROCEDURES

#### 3.1 High Shear Foam Testing

Evaluation of oil lubricants on their foaming tendency under high shear was performed using a 14 speed Osterizer blender. This test is similar to the ASTM test method D 3519 - 88 foam test for aqueous media [43]. The procedure was changed in order to test nonaqueous materials such as the majority of lubricants. This procedure effectively simulated the actual conditions in the application of interest.

This test was developed using samples that ranged from no foaming to excessive foaming in the high shear water vortex found in the marine system. The test differentiated the samples well using the procedure described in section 3.1.1.

A sample volume of 250 ml was tested at room temperature. The sample volume may vary slightly when a series of tests were run with increasing oil concentration. The tests were done using both tap water and salt water. All oil samples tested were insoluble in water. The final screening of all lubricants was done at full blender speed which was reported as 9300 rpm. The blender jar was marked off in 50 ml increments so the amount of foam produced could be estimated. However, the only acceptable result for the purposes of this application was no foam produced.

### **3.1.1 Operating Procedure**

- 1) Clean and rinse blender with tetrahydrofuran (THF), acetone and water. Repeat until no foam is produced blending tap water at full speed.
- 2) Add the required amount of water to the blender using a graduated cylinder. The amount is determined from the desired concentration of the oil-water mixture. The total mixture should have a volume of 250 ml.
- 3) Add the required amount of oil to the blender using a syringe.
- 4) The blender is pulsed several times to disperse the oil in the water. No foam should be produced. If some foam was produced, testing was paused until the foam dissipated.
- 5) Start the blender on the low setting and run for 15 seconds.
- 6) Measure the amount of foam produced.
- 7) If no foam is produced, repeat steps 5 and 6 on the high blender setting.

## **3.2 Friction and Wear Analysis**

### **3.2.1 Standard Four Ball and Three Flats Tests**

The four ball and three flats tests are common tests used to evaluate a lubricant's wear performance. They are effective methods of determining the wear performance of base fluids, additives and greases. There are several variations described below which allow for the analysis of different wear properties of the lubricants.

The four ball test consists of three stationary balls being worn by a fourth ball which is rotating. The geometry of the balls forms a tetrahedron. The conditions that can be altered include: load, speed of rotation, temperature, wear materials, time of test and

lubricant. Both Oils and greases can be evaluated on the four ball test. In the ball on three flats test, the three stationary balls are replaced with disks. Both the four ball and three flats tests evaluate lubricant films in the boundary lubrication regime.

### **3.2.1 A. Apparatus**

Two different four ball machines were used in testing. One is a Falex standard four ball wear test machine and the other is a GE/Brown modified four ball test machine. Each machine has its own advantages.

The Falex machine can handle loads between 1 kg and 60 kg. The speed can be adjusted to either 600,1200 or 1800 rpm. Temperatures used in these studies ranged between room temperature and 200 °C (392 °F). There is also a friction force meter to measure the friction on the rotating ball.

The GE/Brown machine is described in detail by Hsu [44]. It can operate with loads between 1 kg and 160 kg. The loads are applied with a pneumatic piston (10 kg = 3.4 psi). The speed is constant at 600 rpm. The temperature range is similar to the Falex machine. At the time of this study, the device for measuring friction was not functioning correctly and therefore could not be used.

The three lower balls are held stationary in a ball pot as shown in Figure 3.1. A thermocouple is placed in the lower portion of the ball to measure the lubricant temperature. The system is heated with an electric heating block which is directly under the ball pot. On the opposite side of the thermocouple, the ball pot are is connect to the friction force meter.

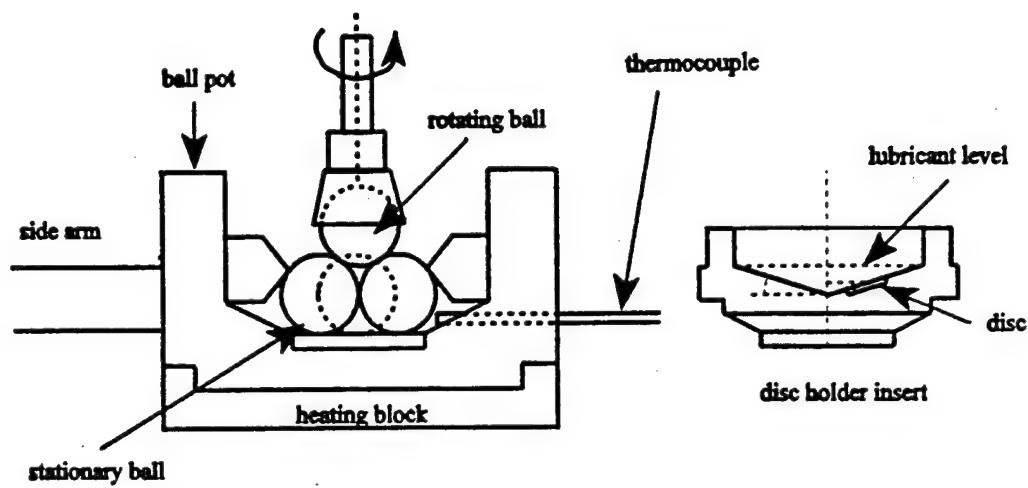


Figure 3.1 Configuration of Wear Specimens in Four Ball Wear Tester

### 3.2.1 B. Wear Specimens

All of the four ball tests were done with a steel on steel system. The steel balls are made of AISI standard steel No. E-52100 with a grade 25 EP polish as described in ASTM test method D 4172-82 [45]. The diameter is 12.7 mm (0.5 in). The Rockwell C hardness is between 64 and 66.

The ball on three flats test were done with a steel top ball as used in the four ball test. Two different material pairs were examined with the disks: steel-on-nickel aluminum bronze (NAB) and steel-on-aluminum alloy (Al 2618 T6). A description of all material properties is given on Table 3.1. The disks are 0.25 inch in diameter and 0.1 inch thick. The disks are held in the ball pot with the aid of the insert shown in Figure 3.1.

The disks are cut from a 0.25 inch rod stock using a diamond tip saw. A small, semicircular grove was filed out of the side of each disk of approximately 0.09 inch (2.3 mm) diameter. Polishing of the flats was done by hand using a polishing jig shown in Figure 3.2. The polishing procedure consisted of 40 figure eight configurations with three unused disks mounted in the polishing jig. All polishing was done using 1200 grit Si-Carbide paper fixed on a flat steel surface. The polished flats were measured with a micrometer to check for uniform thickness. Any deviations in thickness were corrected by hand polishing the flats in a figure eight motion.

Table 3.1 Properties of Wear Materials

Property	Material			
	AISI steel 52100	Al 2618 T6	NAB	C86300
<b>Density (g/cc)</b>	7.78	2.76	7.53	7.7
<b>Hardness</b>	62 -64 RC	115 HB	69.7 RB	225 HB
<b>Young's Modulus (GPa)</b>	207	74.4	110	105
<b>Poisson's ratio</b>	0.29	0.33	0.3	---
<b>Thermal Conductivity</b> $(\frac{W}{mK})$	45.2	170	42	36
<b>Specific Heat</b> $(\frac{J}{kg K})$	456	875	418	376
<b>Chemical Composition (weight %)</b>	Cr: 1.2-1.5 C: 0.95-1.10 Si: 0.20-0.35 Mn: 0.25 - 0.45 P: 0.025 S: 0.025 Fe: balance	Si: 0.1-0.25 Fe: 0.9-1.3 Cu: 1.9-2.7 Mg: 1.3-1.8 Ni: 0.9-1.2 Zn: 0.10 Ti: 0.04-0.10 Al: balance		Cu: 60-68 Mn: 2.5-5.0 Al: 3.0-7.5 Fe: 2.0-4.0 Pb: 0.2 Sn: 0.2 Zn: balance

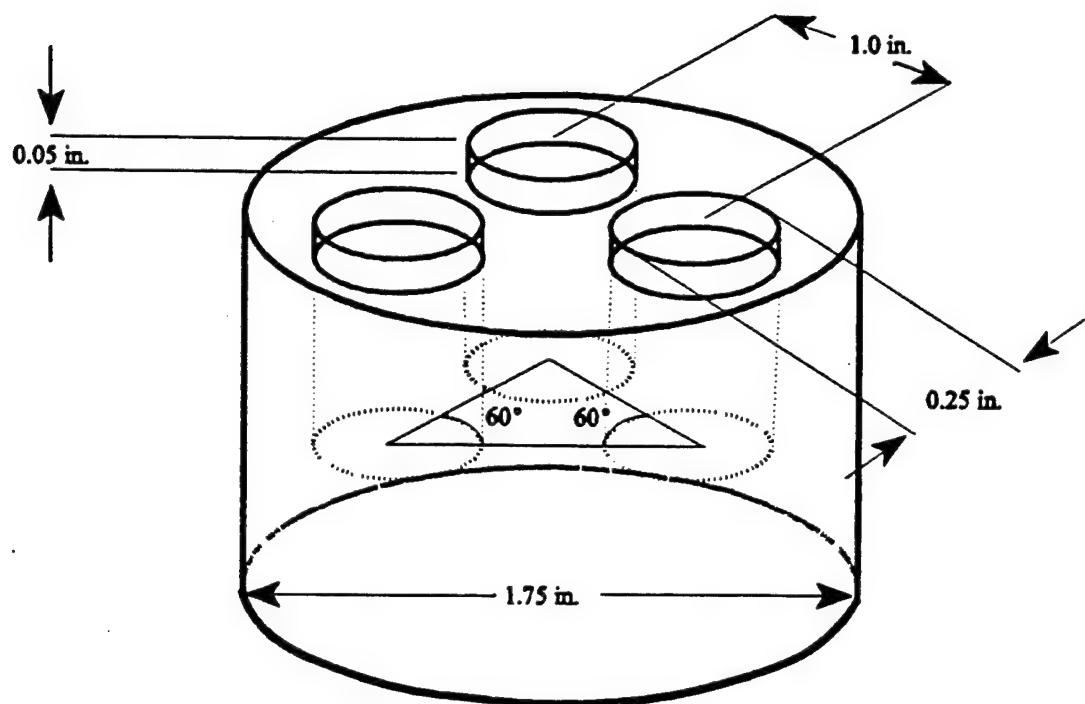


Figure 3.2 Polishing Jig for Ball on Three Flats Wear Specimens

### **3.2.1 C. Oil Four Ball and Ball on Three Flats Procedure**

- 1) All wear test specimens, including the ball pot and its components are washed thoroughly with tetrahydrofuran (THF) and acetone. All components except for the ball pot are put in beakers, filled with THF and then put in a sonic bath for 4 minutes. This is repeated for acetone. A dry air stream is used for drying the components.
- 2) The wear specimens, either balls or disks, are inserted in the ball pot and tightened to prevent sliding. When performing the ball on three flats test, an insert is used to hold the disks. Pins are added to the insert to prevent the disks from rotating. A lint free laboratory wipe is used handling the washed specimens.
- 3) The thermocouple is attached to the ball pot.
- 4) The proper fluid volume is added into the ball pot covering the wear specimens. Approximate volumes are 10 ml for the four ball test and 2 ml for the ball on three flats test.
- 5) The top surface of the heating block and the cavity which holds the top ball chuck are wiped with solvents using a lint free laboratory wipe.
- 6) A ball is placed in the ball chuck and then inserted into the ball chuck cavity and tightened.
- 7) Adjust the drive belt to the proper setting for the desired speed of the top ball.
- 8) Adjust the set point temperature and the time of test to the required values.
- 9) The ball pot is carefully placed under the top ball chuck and onto the heating block
- 10) The desired load is applied and the air bearing is increased until its creates a slight hissing sound.

- 11) Attach chain to handle on ball cup. Rotate ball pot until chain is straight without putting a large force on the chain.
- 12) For a manual start, press the start button once the lubricant has reached the set point temperature.
- 13) Friction force values must be recorded manually as the test is in progress.
- 14) The wear tester will automatically stop at the set time.
- 15) The ball pot is removed and the wear specimens are washed with THF and acetone. In the four ball test, the balls are not removed from the ball pot. In the ball on three flats test, the disks are removed and washed with solvents in the sonic bath before they are replaced in the ball pot. All test specimens are dried with a dry air stream.
- 16) The wear scars diameters of the balls are measured using a microscope with a calibrated scale in the lens. This is the end of the scuffing test mode.
- 17) In the case of a sequential test mode, steps 3-16 are repeated two more times. The first repeat is with the same oil. The second repeat is with a white oil.

[Note: Three drops of oil need to be added to the Falex four ball machine at the beginning of each day. Only one drop of oil is needed for the GE/Brown model.]

### **3.2.1 D. Grease Four Ball Test Procedure**

- 1) All wear test specimens, including the ball pot and its components are washed thoroughly with THF and acetone. All components except for the ball pot are put in beakers, filled with THF and then put in a sonic bath for 4 minutes. This is repeated for acetone. A dry air stream is used for drying the components.
- 2) The ball pot disk is placed in the ball pot. A layer of grease approximately 6-8 mm is spread evenly across the bottom of the ball pot. Three balls are centered on the grease in the ball pot. The top ring is placed on the three balls and pressed down. Grease should begin to flow out of the center of the ring between the balls. Add sufficient grease to form a smooth layer about 3 mm thick over the surface of the balls and across the depressed portion of the ring. The top piece of the ball pot is then screwed in tight to prevent the balls from moving.
- 3) The thermocouple is attached to the ball pot.
- 4) Follow steps 5-14 on the oil four ball test.
- 5) Grease is removed from the top of balls in the ball pot first by wiping out with a paper towel. Then the surface of the balls are washed with solvents until clean.
- 6) The wear scar diameters of the balls are measured using a microscope with a calibrated scale in the lens. The balls remain in the ball pot the whole time.

### 3.2.1 E. Analysis

Wear is measured on the four ball and ball and three flats test by measuring the scar diameter on either the lower three balls or three disks. The wear scars are measured using a microscope with a calibrated scale in the lens. The diameter of the scar is measured in a direction parallel with the wear direction and perpendicular to the wear direction. The average value of the diameter for the three balls is used for analysis.

There are two common methods of reporting the scar diameter used to measure wear. The first is simply the “actual wear scar”. This is the wear scar from the previously mentioned average. The second method is the “delta wear scar”. The delta wear scar is the difference between the actual wear scar and the Hertz scar diameter. The Hertz scar diameter is the average diameter of the indentation caused by deformation of the contact materials under a stationary load [46]. For the four ball test, the Hertz scar can be calculated by the equation:

$$D_h = 8.73 \times 10^{-2} (P)^{1/3} \quad (7)$$

where  $D_h$  is the Hertz diameter in millimeters and  $P$  is the applied load in kilograms.

Calculating the Hertz diameter on the ball and three flats test is done using the following equations:

$$D_h = 2 \times 10^3 * \left[ \frac{3\pi * P_n * (K_1 + K_2) * R_2}{4} \right]^{1/3} \quad (8)$$

$$P_n = 0.408 * P * g \quad (9)$$

$$K_i = \frac{(1 - v_i^2)(10^{-9} GPa/Pa)}{\pi E_i} \quad (10)$$

where:

$P_n$  => normal force on load of one specimen (N)  
 $g$  => gravitational constant ( $g = 9.81 \text{ N/kg}_f$ )  
 $1$  => subscript referring to disk material  
 $2$  => subscript referring to top ball material  
 $R_2$  => radius of the top ball  
 $v_i$  => Poisson's ratio  
 $E_i$  => Young's modulus (GPa)

A delta scar of greater than 0.2 mm is generally defined as scuffing. When performing a one run scuffing test on the four ball, the scuffing load is the first load (to the nearest 10 kg) where scuffing occurs. Sharp increases in wear scars are typical after reaching the scuffing region. This makes repeatability very poor in terms of scar size during scuffing.

The friction coefficient is determined directly from the friction force meter. The friction coefficient for the four ball geometry can be calculated using:

$$f = \frac{0.017 * F}{P} \quad (11)$$

where  $f$  is the friction coefficient,  $F$  is the friction force (g) and  $P$  is the applied load (kg).

### **3.2.2 Grease Extreme Pressure Four Ball**

#### **3.2.2 A. Description**

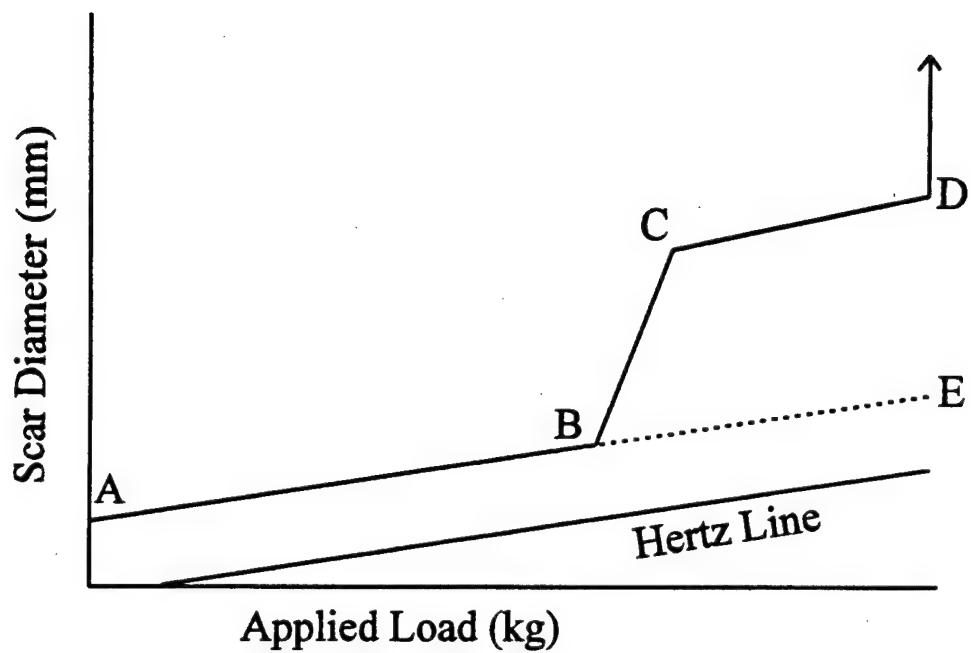
The grease extreme pressure (EP) four ball test is similar to the standard grease four ball test. The primary difference is that the EP four ball is operated at increased loads over the standard four ball test. The geometry is identical to the grease and oil four ball. The EP four ball is run at a rotating speed of  $1770 \pm 60$  rpm for the top ball. The temperature of the grease is  $27 \pm 8$  °C. A sequence of 10 second duration tests are run at increasing loads until the four balls weld together. The procedure is described in detail in ASTM test method D 2596 [46].

#### **3.2.2 B. Analysis**

The grease EP four ball test data is analyzed in a different method than the standard four ball test. The three primary parameters that are determined are described below:

Last Non-Seizure Load (LNSL), kgf - The point where incipient seizure occurs, indicating momentary breakdown of the lubricating film. It is defined as the last load where the scar diameter is not more than 5 percent above the compensation line at that load (See Figure 3.3).

Weld Point (WELDPT), kgf - The lowest load at which the rotating ball welds into the three stationary balls, indicating the EP level of the lubricating grease has been exceeded.



- ABE: Compensation line
- B: Point of last nonseizure load
- BC: Region of incipient seizure
- CD: Region of immediate seizure
- D: Weld point

Figure 3.3 Schematic Plot of Scar Diameter Versus Applied Load

Load Wear Index (LWI), kgf - The load carrying property of the lubricant. It is an index of the ability of a lubricant to minimize wear at applied loads near the weld point. The LWI is the average corrected load of the ten applied loads immediately preceding the weld point. The corrected load is calculated by multiplying the applied load by the ratio of the Hertz scar diameter to the actual scar diameter at the given load.

Larger values of all three parameters are indicative of better wear protection. Figure 3.3 provides a graphical representation of a typical scar diameter versus applied load.

### **3.2.3 Pins on Ring Wear Test**

The pins on ring test was developed to simulate the conditions of the actual system. It consists of two pins being worn on the outer diameter of a large ring. The ring rotates at a high speed (13 m/s) in a heated chamber and steam environment both at 500 °F. Lubricant is applied on the ring before the pins contact the ring in a manner termed "five second prelube". The five second prelube consists of a oil being injected on the disk surface for five seconds at a time beginning ten seconds before the pins are worn for one second. Therefore, there is a five second period immediately before the pins are applied where no additional lubricant is added to the system. The disk is rotating during this whole procedure. Complete details are given in section 3.2.3 A-C.

### 3.2.3 A. Apparatus

The pins on ring wear tester was designed and built by Southwest Research Institute of San Antonio, Texas. The test is run in a sealed chamber as shown in Figures 3.4 and 3.5 [47]. The chamber is maintained at 260 °C with three 240 V, 500 W heaters in the front of the chamber. The steam tank and steam line is also kept at 260 °C (500 °F). During testing, the steam enters the chamber from a valve at the center of the front cover. The ring is rotated at 1995 rpm using a General Electric induction motor. The motor is connected to the drive shaft of the ring by a belt. The speed is reduced to 1995 rpm using different diameter guides for the belt. Lubricant is pumped onto both the top and bottom of the ring with a Haskel pump (pump model: M-71). The load on the pins is applied by pneumatic cylinders with a piston diameter of 1.125 inches. The pressure is supplied from a regulated argon gas cylinder. The apparatus has been described in detail by Kostick [48] with the exception that he used a different motor.

### 3.2.3 B. Wear Specimens

The rings are made of steel ASTM 387 with a diameter of 12.4 cm (4.88 in) and a thickness of 3.2 cm (1.125 in). The Rockwell C hardness of the rings is 76.

Three materials were evaluated for the wear pins: aluminum alloy (Al2618 T6), manganese bronze (C86300), and a nickel aluminum bronze alloy (NAB). A description of the wear materials was shown previously on Table 3.1. The pins range in length from 0.75 to 0.875 inches. The pin diameter is 0.25 inch.

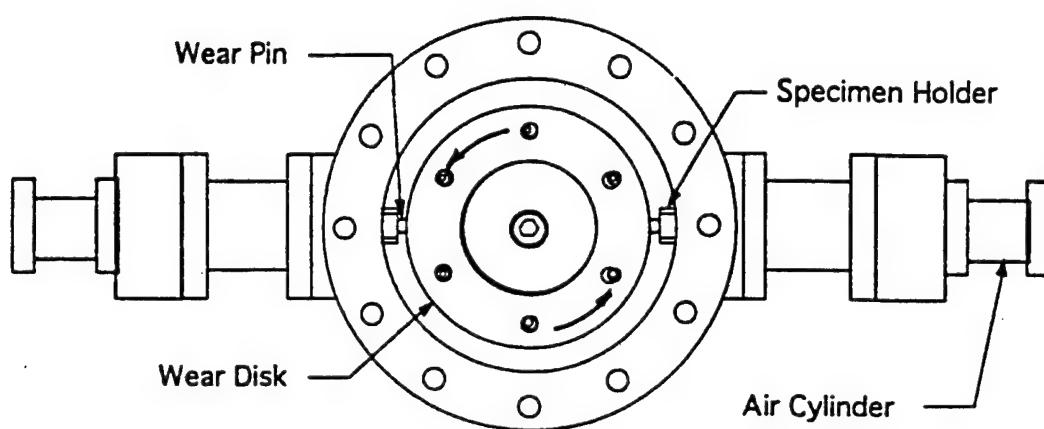


Figure 3.4 Front View of Wear Chamber

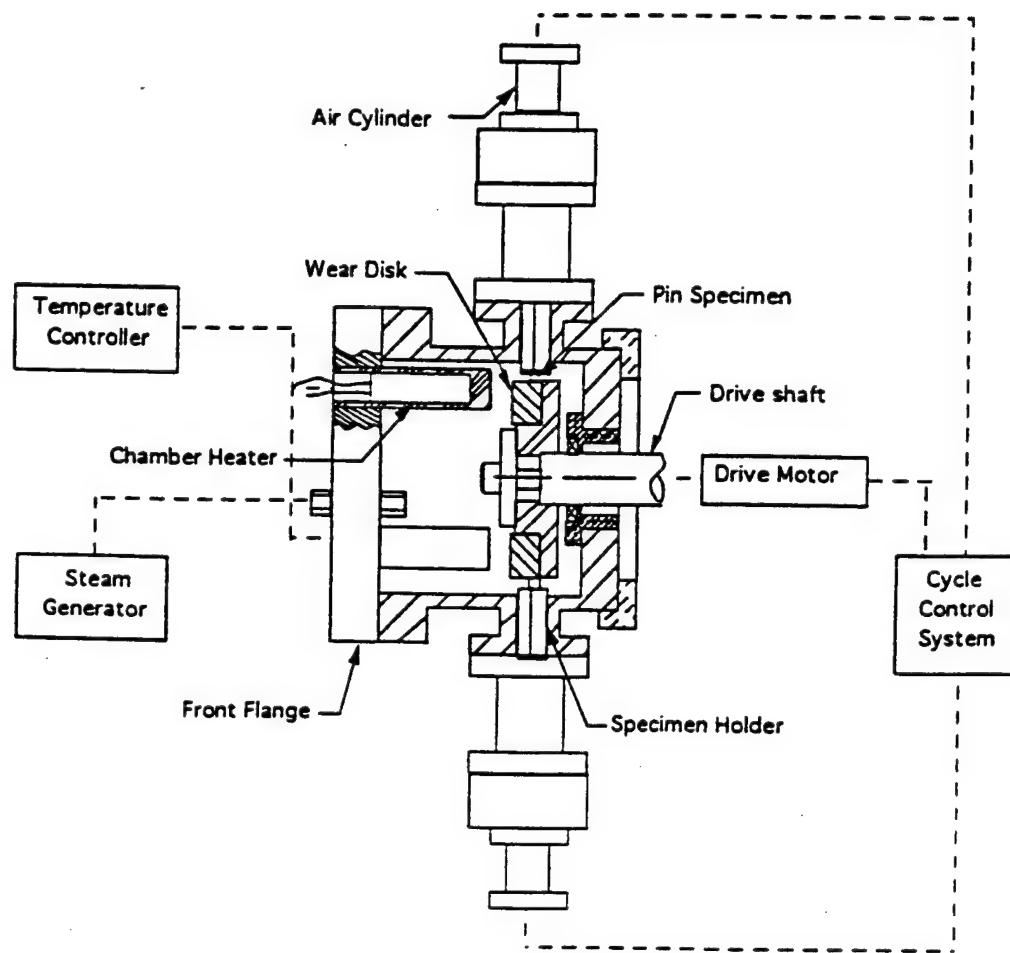


Figure 3.5 Top View Cross Section of Wear Chamber

### 3.2.3 C. Pins on Ring Procedure

- 1) Fill the steam tank with water. Turn on water line and valves leading to the steam tank while leaving the upper release valve open. Fill tank until the water level gage remains on full and there is a steady stream of water flowing out of the release line. Close the release valve and the other water line valves.
- 2) Turn on main power on control monitor and turn on computer screen. The computer should remain on at all times, even after testing.
- 3) The load switch on the control panel should be on manual and in the 'on' position. ('Manual' is to the left and 'on' is the up position.)
- 4) Open the valve on the argon tank.
- 5) Open air line to oil pumping system.
- 6) Adjust pressure for lube on Wilkerson pressure regulator to between 25-30 psi. Note: this does not have to be readjusted every day.
- 7) Clean pins in acetone and weigh to 0.00001 g.
- 8) Clean wear surface on disk with acetone and measure the outer diameter of the disk.
- 9) Insert pins in pin holders inside wear chamber and tighten screws to secure the pins.
- 10) Release the pressure on the pins by pushing the switch on the load box to the right (away from the chamber.)
- 11) Place wear disk in chamber and tighten the six bolts in place.
- 12) Fasten chamber cover using three bolts and connect the chamber thermocouple.

- 13) Adjust load on pins. Open argon tank and set pressure regulator at 38 psi. In 'Chamber Control/Stabilize' menu, check the pressure increase on 'Load 1 Pressure' when the pins are extended (on load box, push switch to the left.) Release pins, adjust pressure regulator and repeat until the pressure increase is 30 psi as read on the screen. This corresponds to 600 psi on the pins. (The screen value times 20 is the actual load in psi.)
- 14) Release pressure on the pins by pushing switch on load box away from the chamber. Then push the switch to the neutral position. On the control panel, turn load switch back to both 'off' and 'auto' position. On load box push switch to the left (towards the chamber).
- 15) Plug the motor into the outlet labeled 'High Speed Motor' and turn the switch to 'hand'.
- 16) Wear in pins and ring: Without lubricant or steam, run pins in a series of one second pulses, 30 seconds apart, until a uniform wear surface is observed on the pins. (For NAB on ASTM 387 steel, four one second pulses were used. For the aluminum pins, a 5 second prelube was used to prevent destroying the pins. A series of 10 one second pulses were used.) This is done at ambient temperature. The control panel under the 'High Speed Wear Test Menu' should appear as follows:

- 2) Specify Shaft rpm (1995)
- 3) Specify Load Duration (1)
- 4) Specify Period Between Load Applications (30)
- 5) Specify Cycling Parameters (current cycle = 1)
- 6) Specify Test Mode (cyclic)

- 17) Turn on steam tank heaters. The switch on front and the button in the back must both be turned on.
- 18) Do not let pressure in steam tank exceed 600 psi. When the pressure reaches 600 psi open the release valve to maintain the pressure near 600 psi.
- 19) Remove pins and disk and clean them as done previously. (To remove the disk it may be necessary to switch the load back to manual and release the pressure on the load box.) Weigh the pins. Replace the pins and disk in the wear chamber and fasten chamber cover.
- 20) Plug in heater for steam line on top of the steam tank heater controller. The set point should be between 500 and 525 °F.
- 21) Turn on chamber heaters on control panel. Chamber test temperature is 500 °F or 260 °C. Set chamber temperature set point to 270 °C in chamber control/stabilize menu.
- 22) In the 'High Speed Test Menu', change 'Cycling Parameters' to begin at 1 and end at 5. Change the 'Period Between Load Applications' to 120 (seconds).
- 23) Check load on pins as done in steps 13 and 14.
- 24) When the steam, chamber and steam line have all reached the desired temperature, the test may begin. Open the valve from the steam tank to the steam line. The motor is turned on by turning the outlet switch to 'hand'.
- 25) On the control screen, select "Run High Speed Test" on the High Speed Wear Test menu. Press 'Enter'. This time marks 15 seconds prior to the time of pin contact.

- 26) The steam valve into the chamber is opened manually 12 seconds before the pins contact. Lubricant is manually turned on 10 seconds before the pins contact and turned off 5 seconds before the pins contact. (This is referred to as "five second prelube".) The steam is turned off after the pins contact. This will be repeated a total of 5 times. A 'click' is audible 15 seconds before the pins contact to serve as a warning.
- 27) After the last pulse, turn off the motor, chamber heater and close the valve from the steam tank. Open the steam valve on the chamber cover to purge the steam in the line and then close the valve. Remove the pins and disk from the wear chamber.
- 28) Clean the pins and disk in acetone. Weigh the pins.
- 29) Repeat steps 21 - 28 until a uniform wear rate is observed. A minimum of four trials should be done with lubricant. The last four trials are used to calculate the wear rate.

### **3.2.3 D. Analysis**

The primary method for evaluating the wear rate is the volumetric pin material lost per unit sliding distance. This is calculated by measuring the weight loss of the pins after every five, one-second pulses and then using the density to convert to volume. A minimum of four points are used in determining the wear rate after steady state wear is observed. This ignores the initial wear in of the pins. A least squares fit is used to fit the steady state points on a graph of volume lost versus sliding distance. The slope of this line is the wear rate. The wear rate is determined for each separate pin and then as an overall average wear rate. A sample plot of the volume lost versus sliding distance is shown in

Figure 3.6. In this example, the lines are simply joining the points and are not the least squares fit.

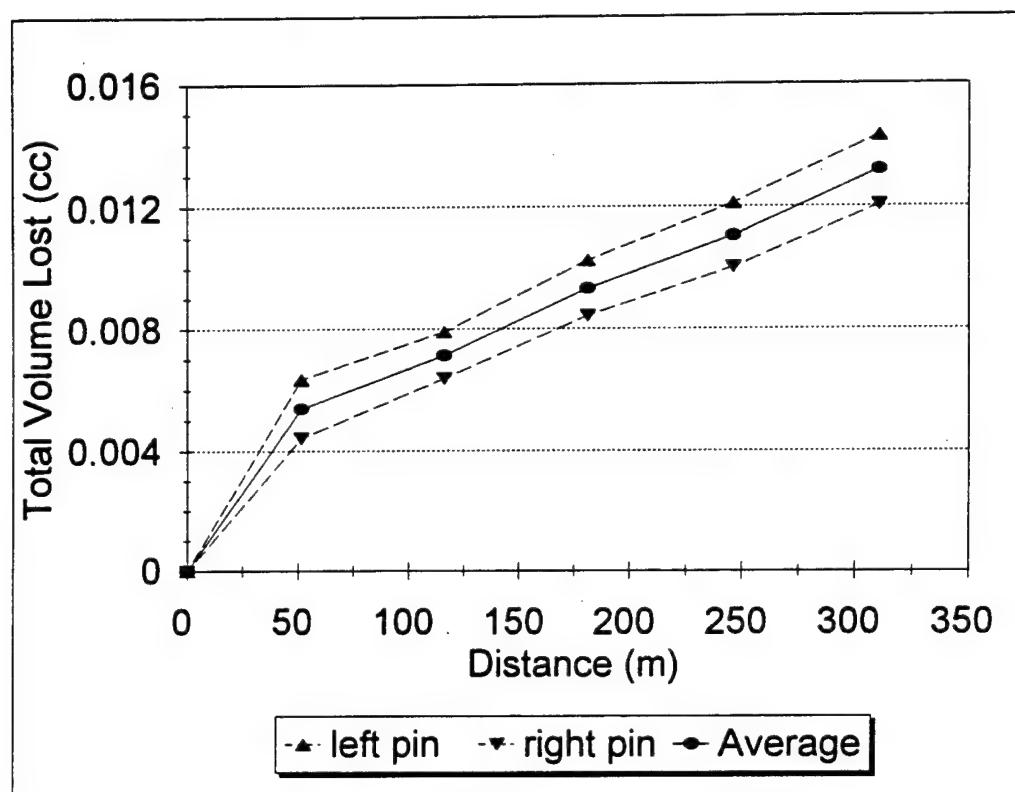
### **3.3 Oxidation and Thermal Stability Analysis**

#### **3.3.1 Penn State Microoxidation Test**

The Penn State microoxidation or microreactor test was designed as a rapid method to evaluate stability of lubricants and additives and later adapted for use with greases [49, 50]. This is a thin film test enables a comparison of both volatility and oxidation stability of a fluid. Test temperature and duration are adjusted to simulate desired conditions. The oxidation testing also requires the use of gel permeation chromatography.

#### **3.3.2 Apparatus**

The Penn State micro-reactor design is described in detail in numerous publications [51, 52, 53]. A brief summary of the micro-reactor design will be given here. A low carbon steel test cup is placed in a glass reactor and set in a bath at the desired temperature. The test cup and reactor are shown in Figure 3.7. For temperatures of 150 °C or lower an oil bath was utilized for temperature control. Above 150 °C, a hot metal bath was used. Dry air flows through the reactor at a rate of 20 cc/min. The air flow is directed onto the lubricant surface and then exits near the top of the reactor.



Lubricant: MO1  
Material: NAB  
Load: 600 psi  
Atmosphere: Steam 500 F

Figure 3.6 Sample Pins on Ring Plot

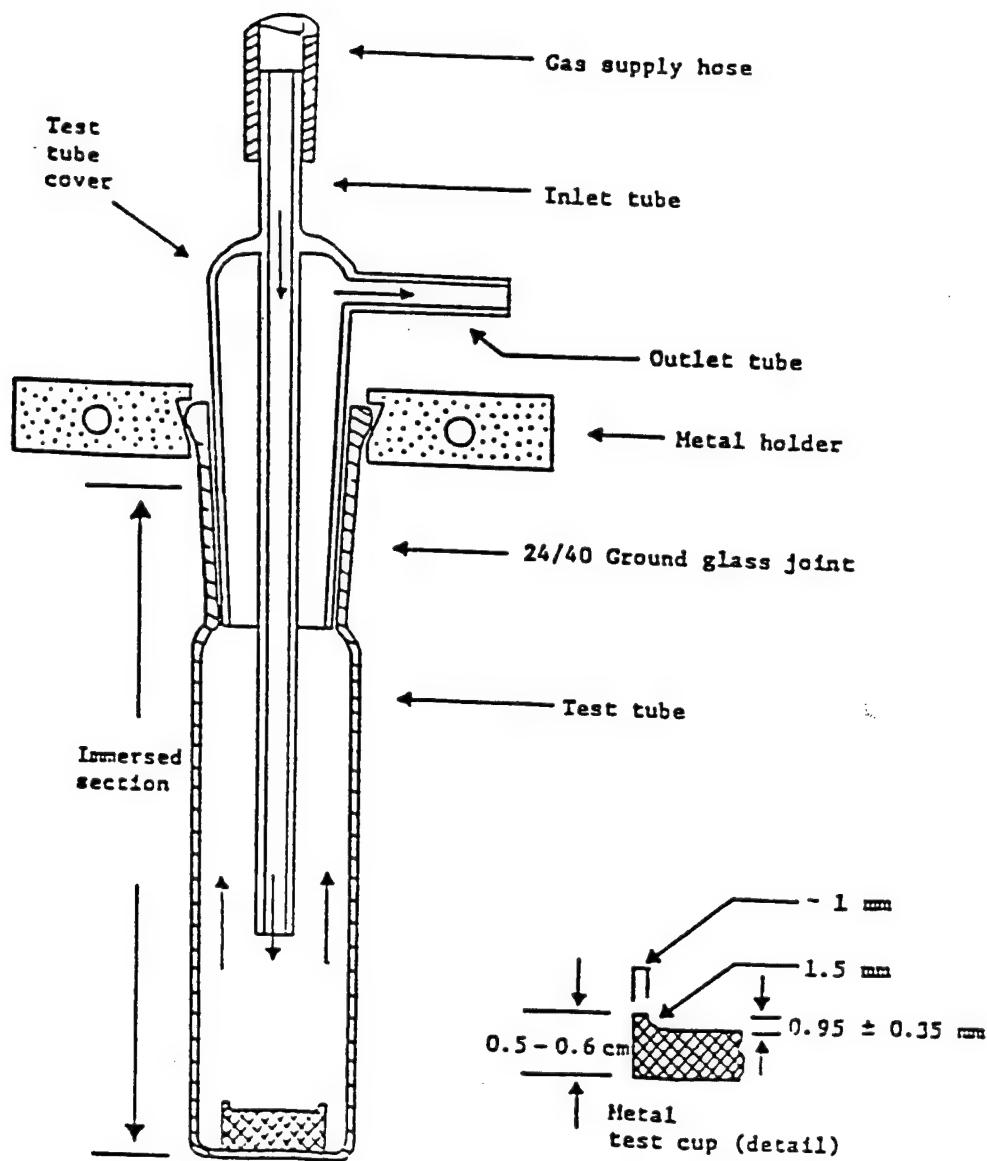


Figure 3.7 Penn State Microoxidation Test Apparatus

### 3.3.3 Oil Microoxidation Procedure

- 1) A fresh surface on the metal catalysts are ground smooth before each test. The catalysts are stored in benzene until the day before testing.
- 2) The day before the test, a wire is fastened around the catalyst to ease in handling and later for inserting the catalyst in the reactor. The catalysts are washed with THF and dried with an air stream. They are then stored overnight in separate 1 oz wide mouth jars filled partially with Drierite.
- 3) On the day of the test, the catalysts with the attached wire are weighed on a Metler 6 digit microbalance. After each weighing, a 10 g standard is weighed to calibrate the measurements.
- 4) The glass reactors are washed with soap and water and then with THF. They are dried first with an air stream and then by heating in an oven at 120 °C for a minimum of 10 minutes. Also, 100  $\mu$ L syringes with 21 cm needles are cleaned with THF and dried by a dry air stream.
- 5) Both nitrogen and air lines are adjusted to flow rates of 20 cc/min. A soap bubble flow meter is used for this purpose.
- 6) Metal holders are fastened on to the glass reactors, a catalyst is inserted in each and then the reactors are placed in the constant temperature bath set at the desired temperature.
- 7) While the reactors and catalysts are reaching thermal equilibrium with the baths, the reactor is purged with a nitrogen for 30 minutes. This is followed by an air flow for 10 minutes.

- 8) The 100  $\mu$ L syringes are filled with the oil samples using an eyedropper. The plungers on the syringes are inserted and then release all but 40  $\mu$ L. The tip of the syringe is wiped clean with a laboratory wipe to ensure consistent sample size.
- 9) The sample is injected onto the catalyst surface by quickly removing the air line and injecting the sample with the syringe. Then air line is then replaced. This is the start time (t=0).
- 10) At the end of the desired test time, the reactors are removed from the bath and placed in an air stream for cooling.
- 11) After cooling, the catalysts are removed from the reactors and stored overnight in the 1 oz jars with Drierite.
- 12) The following day, the catalysts with the remaining oil are weighed to determine evaporation/volatility.
- 13) The catalyst are inserted in a clean 1 oz bottle and 5 ml of THF are injected along the walls of the bottle to dissolve the remaining oil without washing off any deposits.
- 14) After 10 minutes, the THF/oil solution is removed with a syringe and saved. Step 13 is then repeated once more.
- 15) Once dry, the catalyst with deposits is weighed again to determine the amount of deposit.
- 16) The 10 ml of THF/oil solution can be analyzed with gel permeation chromatography (GPC) to determine the percentage of high and low molecular weight products.

### 3.3.4 Grease Microoxidation Procedure

The grease microoxidation procedure is similar to the oil procedure with a few exceptions due to the properties of greases. The procedure is described in detail by Dholakia [54]. The oxidation system is identical to the one described previously for oils except that the 125 °C environment is maintained with an oil bath. The main differences between the grease and oil test procedure will be explained here briefly.

One difference is a 40 milligram sample of grease is applied evenly on the test cup prior to being placed in the reactor and temperature bath. Nitrogen is passed through the reactor for 30 minutes while the system reaches thermal equilibrium. The test time starts when the nitrogen flow is switched to air flow. The second major difference is that once the oxidized grease is dissolved in THF, the slurry must be filtered to remove the soaps or other thickeners found in greases. Filtering is done using a 25 mm diameter Millipore filter with a pore size of 0.2 micrometers while 25 psi of nitrogen is being applied. The resulting solution can then be analyzed in the GPC.

### 3.3.5 Analysis

Generally, four values are determined from the PSU microreactor test: 1) percent evaporation 2) percent deposit 3) percent same molecular weight (SMW) 4) percent high molecular weight (HMW).

The percent evaporation is calculated directly from the weights of the catalyst with sample before testing and the weight of the catalyst and remaining sample after testing. In the case of oils, the weight of sample before testing is found using the volume injected and

the oil's density. The percent deposit is the difference between the dry catalyst before testing and the catalyst with deposits after the lubricant has been removed with the THF. None of the greases examined in this study were found to have deposits.

The percent same molecular weight and percent high molecular weight are calculated from the results of the GPC as shown in Figure 3.8. A comparison between the oxidized lubricant and an original sample allows for the determination of HMW and SMW. The printouts from the GPC of the two samples are overlaid on each other. The percent HMW and SMW are calculated using the ratio of areas of the two samples. The area of the oxidized sample that remains inside the area of the original sample is considered SMW. The portion of the oxidized sample that has a higher molecular weight becomes HMW. It should be noted that SMW accounts for both unoxidized lubricant and also oxidized products that still fall in the same molecular weight range. The unoxidized and oxidized products can be separated with the use of a clay percolation column and a GPC as described in ASTM test method D 2007 [55].

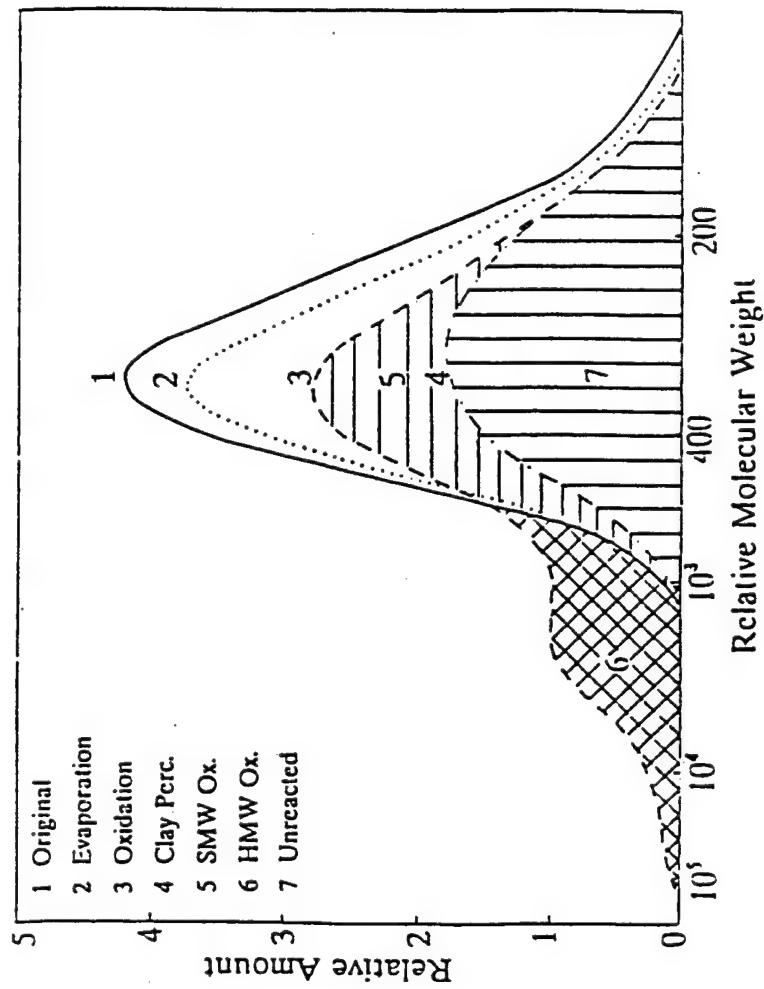


Figure 3.8 Typical GPC Analysis Plot

## Chapter 4

### OIL RESULTS AND DISCUSSION

#### 4.1 Test Fluids

##### 4.1.1 Oil Base Fluids

Polyalkylene glycols were chosen as the base fluid for the lubricant that would replace the currently used mineral oil (MO1). The decision to use polyalkylene glycols was based on previous studies on the same application. The previous studies focused on water soluble polyalkylene glycols which are those that contain a significant amount of ethylene oxide in the backbone of the chain. These fluids were found to have foaming problems when the aqueous mixtures were not in a heated system. Insoluble polyalkylene glycols formed from strictly propylene oxide as the chain building blocks were evaluated in this research to prevent this foaming problem in a water mixture. Some of the polypropylene glycols are even used as antifoam agents in several applications [56].

Physical properties of these base fluids are given in Table 4.1.

##### 4.1.2 Oil Additives

In addition to finding an appropriate base stock, certain additives would be needed to improve the performance characteristics of the base fluid. The additives would have to be compatible with the base fluid, remain in solution and would not adversely effect any other additives when used in combination. Any additives that were incompatible with the

Table 4.1 Physical Properties of Test Lubricants

Lubricant	Average Molecular Weight	Viscosity (cSt)		Viscosity Index	Specific Gravity (20/20 C)	Pour Point (C)
		100 C	40 C			
<b>Mineral Oils</b>						
MO1	1500	25	303	104	0.887	< 18
MO2		16.3-21.9	220-250 (SAE 50)			
<b>Polyalkylene Glycols (100% propylene oxide)</b>						
PPG1	640	5.65	26.5	161	0.981	-48
PPG2	1550	21.4	124	200	1.000	-32
PPG3	2080	36.9	227	214	1.002	-29
PPG4	2490	51.9	338	219	1.002	-23
<b>Polyalkylene Glycol (50:50 ethylene oxide:propylene oxide)</b>						
PEPG1	1590	25.6	132	230	1.051	-34
<b>Polyalkylene Glycol (75:25 ethylene oxide:propylene oxide)</b>						
PEPG2	2470	41.5	282	207	1.099	4

base fluids or combinations of additives that would form a precipitate were eliminated from consideration. The additives that proved compatible with the polyalkylene glycols evaluated here are presented in Table 4.2.

#### 4.2 Oil Viscosity

One requirement of replacement lubricant was to have a similar viscosity of the current mineral oil, particularly at the approximate operating temperature of 350 °F. Using the polyalkylene glycols listed on Table 4.1, fluids viscosities were extrapolated to 350 °F with the aid of ASTM viscosity charts for petroleum products [57]. The viscosity charts were accurate enough since only an approximate viscosity match was required. The projected viscosities of the neat (no additives) lubricants are shown on Table 4.3. Of the polypropylene glycols, PPG 2 is shown to have the most similar viscosity to MO1 at the operating temperature.

Several blends of polyalkylene glycols were also made to approach the MO1's viscosity at 350 °F. The components of the blends are shown below in Table 4.4:

Table 4.4 Components of Polyalkylene Glycol Blends

Blend 1: 88 % PPG 2 + 12 % PPG 1

Blend 2: 50 % PPG 2 + 50 % PPG 1

Blend 3: 30 % PPG 2 + 30 % PPG 1 + 40 % PPG 3

Blend 4: 80 % PPG 2 + 20 % PEPG 2

Note: All percent values refer to weight percent

Table 4.2 Polyalkylene Glycol Additives and Common Use

Additive	Nomenclature	Common Use	Supplier
tricresyl phosphate	TCP	anti-wear	-----
diisopropyl acid (hydrogen) phosphite	DIAP	anti-wear/EP	Albright & Wilson
butanediol ethoxylated phosphate ester	PE1	anti-wear	Rhone-Poulenc
dodecylalcohols ethoxylated phosphate ester	PE2	anti-wear	Rhone-Poulenc
ethoxylated polyoxypropylene	POP	anti-wear	Rhone-Poulenc
nonionic alkyl phosphate ester	PE3	anti-wear	Akzo Nobel Chemicals
copper oleate	Cu	anti-oxidant	Mooney Chemicals
octylated N-phenyl-1-naphthylamine	PNA	anti-oxidant	Ciba-Geigy
Thiodiethylene bis(3,5-di-tert-butyl-4-hydroxyhydrocinnamate)	TBP	anti-oxidant	Ciba-Geigy
octylated butylated diphenylamine	DPA	anti-oxidant	King Industries

**Table 4.3**      **Neat Lubricant Projected Operating Viscosity**

<b>Lubricant</b>	<b>Projected Viscosity at 350 °F (177 °C) (cSt)</b>
MO1	5.6
PPG1	2.0
PPG2	5.4
PPG3	9.5
PPG4	12.5
PEPG2	10.5

The blend viscosities were estimated with viscosity blending charts [56] and then with standard viscosity charts as mentioned with the neat polyalkylene glycols. The projected viscosities of the blended lubricants are shown on Table 4.5. Blends 1 and 3 project viscosities even closer to MO1 than PPG2, however, the difference is minimal. Blend 4 is a combination of water soluble and insoluble polyalkylene glycols. This blend was developed for two reasons: 1) increase the biodegradability of the base stock with the addition of the water soluble fluid 2) test the ability of PPG2 to prevent foaming of the water soluble fluid. Blend 1, blend 3, blend 4 and neat PPG2 would all be examined further as potential base stocks.

#### 4.3 High Shear Foaming Test Results

Base line testing for each pure polyalkylene glycol and several blends were tested using the high shear foaming test. Initial samples consisted of 10 ml lubricant in a 250 ml mixture with tap water. The tests were run at low speed and then if no foam was produced, the tests were repeated at high speed. None of the fluids examined in this study were found to produce foam at the high speed if they did not produce foam at the low speed. Since any foam at all at either speed was considered unacceptable for this application, lubricants producing foam at the low speed were not tested at the higher speed.

The foaming test results of the neat polyalkylene glycols and blends are given on Table 4.6. The lighter two polypropylene glycols, PPG1 and PPG2, did not create any foam. The two heavier polypropylene glycols, PPG3 and PPG4, created a thin layer of

**Table 4.5      Blended Lubricants Projected Operating Viscosity**

<b>Lubricant</b>	<b>Projected Viscosity at 350 °F (177 °C) (cSt)</b>
Blend 1	5.5
Blend 2	2.6
Blend 3	5.5
Blend 4	6.7

**Table 4.6 Foaming Results on Polyalkylene Glycol Base Fluids**

Base Fluid	Amount of Base Fluid (ml)	Initial Amount of Foam (ml)	Amount of Foam after 2 min (ml)
PPG1	10	0	0
PPG2	10	0	0
PPG3	10	10	0
PPG4	10	10	0
PEPG1	10	200	80
PEPG2	10	50	0
Blend 1	10	0	0
Blend 3	10	0	0
Blend 4	10	0	0
FF PPG	10	0	0

foam across the mixture surface. Repeat testing at the high speed produced similar results. The difference in the lower and the higher molecular weight polypropylene glycols is likely a function of the longer chain molecules with a higher viscosity being slightly more stable in a foam. High viscosity fluids will resist drainage from the bubble walls to the bulk fluid more than lower viscosity fluids. This fluid drainage from the bubble surface is a principle mean by which a foam is broken down.

The two neat fluids that were water soluble due to the oxyethylene groups both showed significant foaming. The foam produced from PEPG 1 had still not broken down after two minutes. The foam from PEPG 2 all dispersed in approximately 15 seconds. A potential explanation of the difference in the two fluids is the greater affinity of PEPG 2 to water due to the higher concentration of oxyethylene in the molecules. This possibility was not explored due to the desire for a non-foaming lubricant.

Three blends were also tested in the high shear foam test also shown on Table 4.6. The results of blend 1 and 3 not producing foam was expected due to the low or no foam created in testing of the individual lubricants. The fact that blend 4 did not foam confirms that high concentrations of PPG2 can prevent foaming of fluids that are known to foam (PEPG 2). However, testing of blend 4 was discontinued due to the manner the lubricant is introduced to the high speed water vortex in the application of interest. The water solution sent through the vortex is pumped from a large holding tank containing water and lubricant. The solution is pumped from the bottom of the tank meaning that it is likely that little if any of PPG2 would be pumped through the vortex while a relatively high concentration of PEPG 2 would be pumped through. Due to this system design, blend 4

was eliminated as a potential replacement base fluid.

Low concentrations of PPG2 and PPG1 were tested as a result of the system design mentioned above. These tests were performed by adding the lubricant 1-2 drops at a time into 250 ml of water and running a high shear foam test after the addition of each drop. PPG1 was tested between 1 and 16 drops of fluid which corresponds to approximate concentrations of 0.02-0.4 weight percent. No foam was observed at any of these concentrations. PPG2 was tested at concentrations ranging from 0.02 - 9.4 weight percent. When one drop was added to 250 ml and then a total of two drops were added (approximate concentrations of 0.02 and 0.04 weight percent respectively), a thin ring of tiny bubbles approximately 1 mm in diameter formed around the wall of the blender and then dispersed almost immediately. The ring of bubbles was only 1-2 mm high and no more than 2 mm wide. This total foam volume produced was less than 1 ml. This low level of foam dispersed immediately and was not considered to be a potential problem. The addition of 3 drops of PPG2 in a 250 ml water mixture (approximate concentration of 0.06 weight percent) did not produce any foam. Subsequent tests ranging to a concentration of 9.4 weight percent did not create any foam.

Based on the excellent results of PPG2 and its similar viscosity to MO1 at the operating temperature, PPG2 was chosen as the primary base fluid for continued testing. Blends 1 and 3 were not considered further since they did not offer a significant advantage over the neat PPG2.

All the additives that were considered for use in the polyalkylene glycols were tested in PPG2 in a wide range of possible concentrations. None of the additives shown

on Table 4.2 created foam at any concentration levels that were chosen as reasonable in PPG2 as suggested by manufacturer's recommendations.

Based on wear and oxidation testing, the following combination of additives were added to PPG2: 0.5 weight percent DIAP, 1.0 weight percent PNA and 1.0 weight percent TBP. This will be referred to as the "fully formulated oil" or "FF PPG". This FF PPG had identical results as the PPG2 base fluid.

#### **4.4 Oil Wear Test Results**

Wear testing on the PPG2 based lubricant was done with the four ball wear test, the ball on three flats test and the pin on ring test. The results of these three wear tests gives an evaluation of wear additive performance on the different wear materials. As described previously, wear materials evaluated include: AISI steel 52100, NAB, Al 2618 T6 and steel 387. The material properties were shown previously in Table 3.1. NAB is not currently in the actual operating system, but it is under consideration to improve wear in certain areas.

##### **4.4.1 Four Ball Test**

A screening of wear additives was accomplished using the four ball wear test. Both the sequential four ball and the scuffing test modes were implemented. All four ball tests were AISI steel 52100 on steel wear pairs. For all the oils tested, the temperature was 75 °C and the rotating speed of the top ball was 600 rpm (23 cm/s).

#### 4.4.1 A. Sequential Four Ball

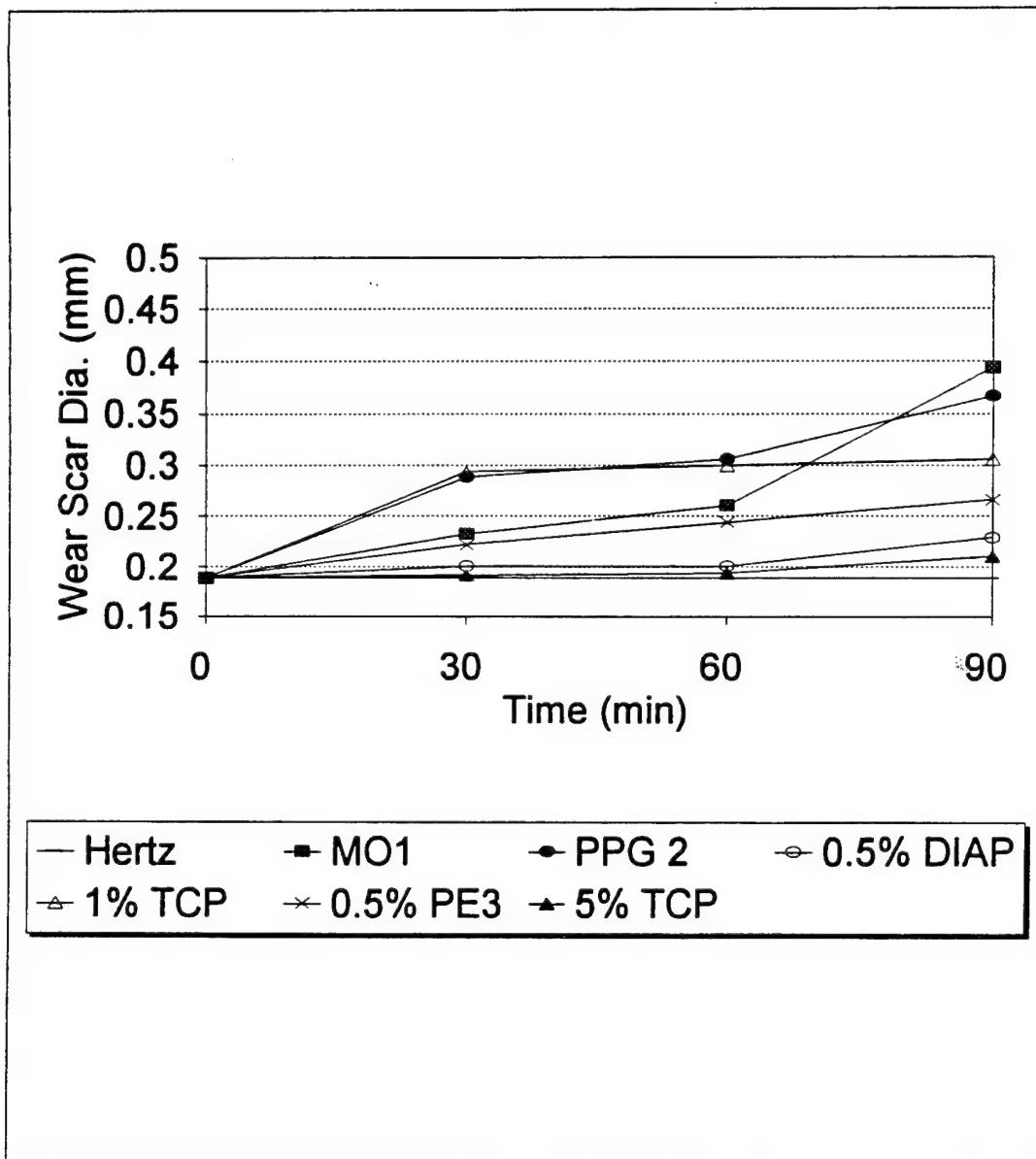
The sequential four ball was run at a 10 kg load for three 30 minute intervals. The test fluid is added the first two runs and on the third run a white oil (highly refined mineral oil) is used. The white oil does not contain any additives. Its purpose is to determine whether or not the test lubricant has built a protective film or coating on the contact area that will provide protection after the bulk lubricant has been removed.

The anti-wear additives were added in concentrations recommended by the manufacturer or concentrations from previous work. The results for a series of additives in the PPG2 as well as the regular mineral oil are shown in Figures 4.1 and 4.2. The neat PPG2 is shown to be significantly less effective than MO1 in wear protection. This result clearly displays the need for an anti-wear additive.

It is apparent that 0.5 weight percent DIAP and 5 weight percent TCP show the best protection. In both cases, the wear on the third run with the white oil increased only slightly indicating both additives provide a protective film which does not need continual replacement from the bulk lubricant. This is in stark contrast to the mineral oil which showed a sharp increase in the wear scar on the third run with the white oil. Further testing focused primarily on DIAP and TCP additives due to their excellent performance on this test.

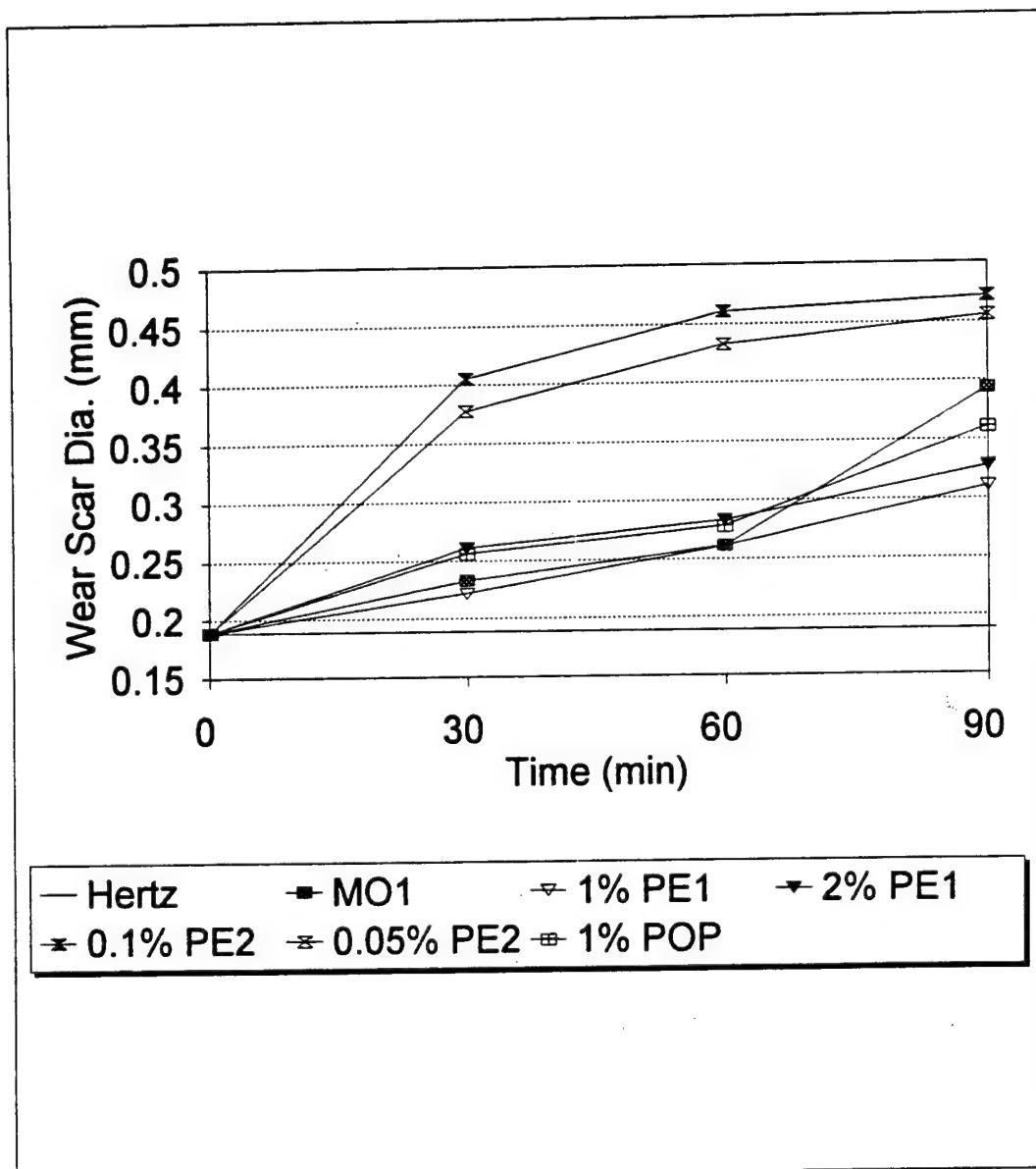
The other two additives which showed wear similar or less than MO1 are 0.5 weight percent PE3 and 1.0 weight percent of PE1. From Figure 4.2, the additive PE2 is seen to be corrosive with increasing concentration under the specified conditions.

The FF PPG was tested for one 30 minute the same conditions as the other loads



Base Oil: PPG2      Balls: steel 52100  
Temperature: 75 C      Speed: 600 rpm  
Load: 10 kg

Figure 4.1 Sequential Four Ball Results (A)



Base Oil: PPG2      Balls: steel 52100  
Temperature: 75 C      Speed: 600 rpm  
Load: 10 kg

Figure 4.2 Sequential Four Ball Results (B)

to test for adverse affects of the combined additive package on a steel on steel system. The results are shown in Table 4.7 along with PPG2 with 5.0 weight percent DIAP and MO1. It is apparent that the addition of the antioxidant additives does not alter the performance of the DIAP in PPG2.

#### **4.4.1 B. Scuffing Four Ball**

The scuffing test is a series of one run four ball tests employed to determine the load (to the nearest 10 kg) where scuffing occurs. Scuffing is defined as a delta scar of greater than 0.2 mm as mentioned earlier. The load is increased in 10 kg intervals over a series of tests until the balls are scuffing. A 30 minute test time is standard for all runs. The scuffing test gives an idea of the load carrying capacity of an oil. Higher scuffing loads are indicative of better lubrication properties at high loads.

Scuffing tests were run on were run on MO1, neat PPG 2, and PPG 2 with either DIAP or TCP. Table 4.8 contains the average results from these tests. The two lubricants with the best performance were the mineral oil and the PPG2 with 0.5 weight percent DIAP. The mineral oil shows a sharp jump in delta wear scar from 70 to 80 kg. At the 80 kg load, MO1 is drastically scuffing. PPG2 containing DIAP also begins scuffing at 80 kg, but it has just barely exceeded the 0.2 mm delta scar commonly defining scuffing. The PPG2 with 5 weight percent TCP was found to scuff at 60 kg. The PPG2 containing TCP actually performed worse than the pure PPG2. TCP is an antiwear additive which provides wear protection only at lower loads. It is not capable of forming an adequate protective film at higher loads as the data indicates.

**Table 4.7 Fully Formulated Oil on Four Ball Test**

Conditions: Temperature: 75 °C  
Load: 10 kg  
Speed: 600 rpm

<b>Lubricant</b>	<b>Actual Wear Scar (mm)</b>
FF PPG	0.206
PPG2 + 0.5%DIAP	0.206
MO1	0.233

Table 4.8 Four Ball Scuffing Results

Base Oil: PPG2 Speed: 600 rpm  
Material: Steel 52100 Temperature: 75 C  
Time: 30 min

### DELTA SCARS (mm)

(actual scar minus hertz scar)

Lubricant	Loads (kg)		
	60	70	80
MO1	0.128	0.128	<b>0.500</b>
PPG2	0.156	<b>0.245</b>	
0.5% DIAP		0.191	<b>0.222</b>
5% TCP	<b>0.312</b>	<b>0.295</b>	

Note: Numbers in bold indicate scuffing (delta scar > 0.20 mm).

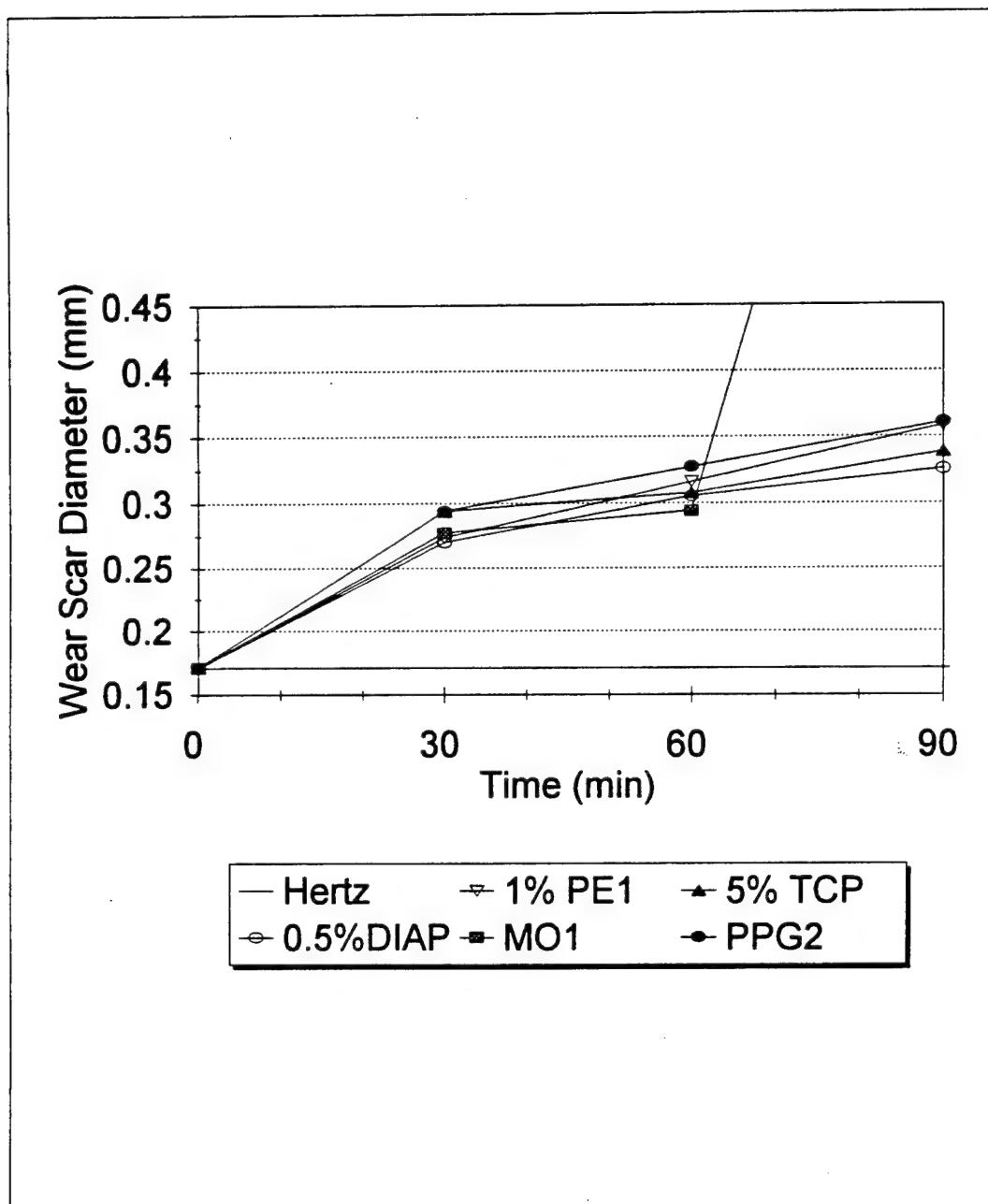
#### **4.4.2 Ball on Three Flats Test**

The ball on three flats tests is very similar to the four ball test. The principle advantage of the ball on three flats test is the ease in testing wear material combinations that are not readily available as 0.5 inch ball bearings. AISI steel 52100 was always the top rotating ball material in the ball on three flats tests described here. The disk materials tested were Al 2618 T6 and NAB whose properties were given in Table 3.1. For all ball on three flats tests, the temperature was maintained at 75 °C and the top ball rotated at 600 rpm (23 cm/s).

##### **4.4.2 A. Steel on Aluminum**

A sequential ball on three flats test was used to test steel on aluminum wear characteristics. The sequential test mode is the same as with the sequential four ball test. Using the same wear disks, two runs of 30 minutes are made with the lubricant being evaluated. The third run is done with white oil. The disks are locked in place with the use of a pin which prevents the disks from rotating and ensures identical placement on subsequent runs.

The steel on aluminum system was initially ran with a load of 2 kg. The results, as shown on Figure 4.3, were grouped so closely together it was decided to increase the load in order to get a wider spread in the results. The one piece of evidence that can be seen clearly from this data is the inability of MO1 to protect against wear after it has been replaced with the white oil on the third run. This result matches the results of the four ball tests.



Materials: Steel 52100 on Al 2618 T6

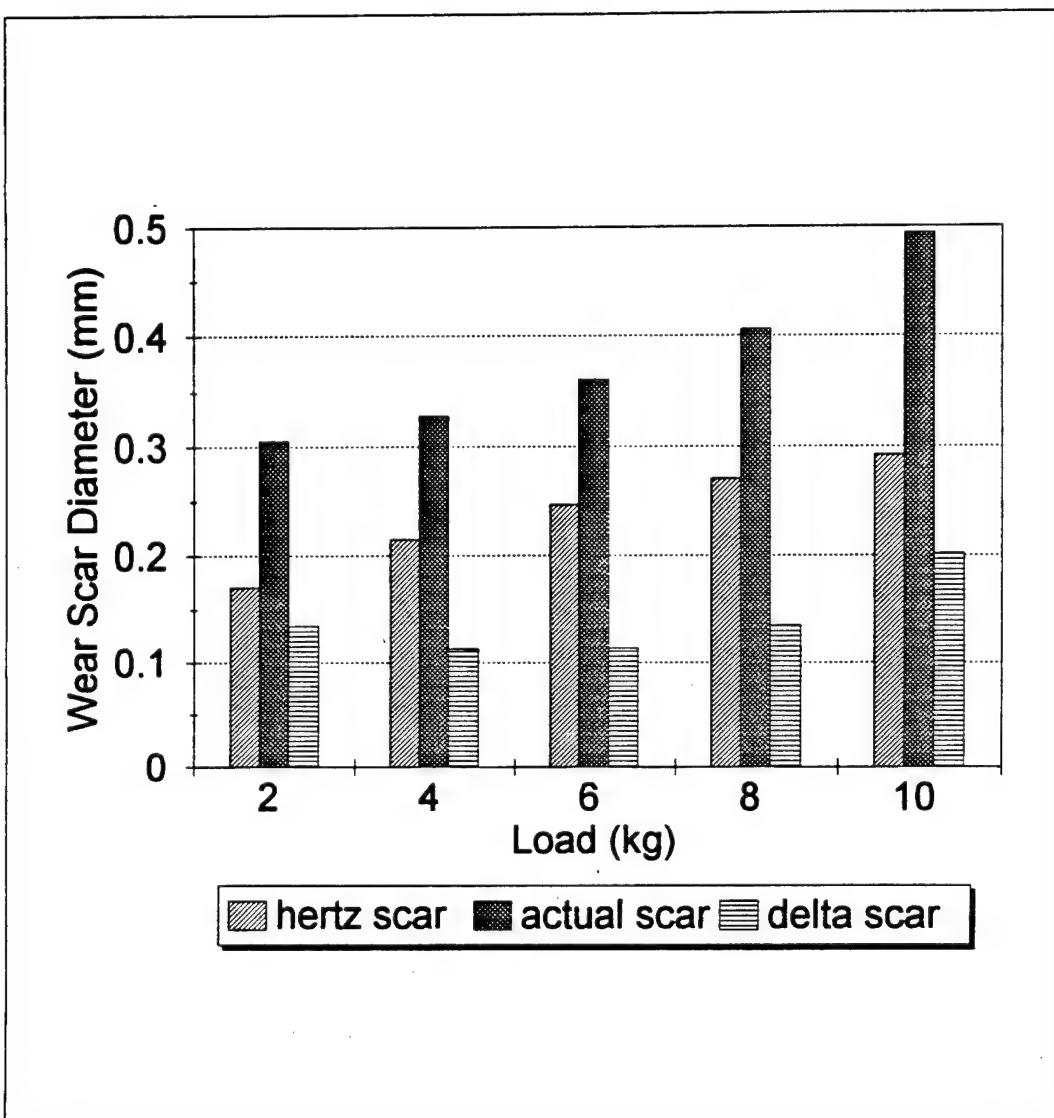
Load: 2 kg  
Temperature: 75 C

Base Lubricant: PPG2  
Speed: 600 rpm

Figure 4.3 Sequential Ball on Three Flats for Steel on Aluminum at 2 kg

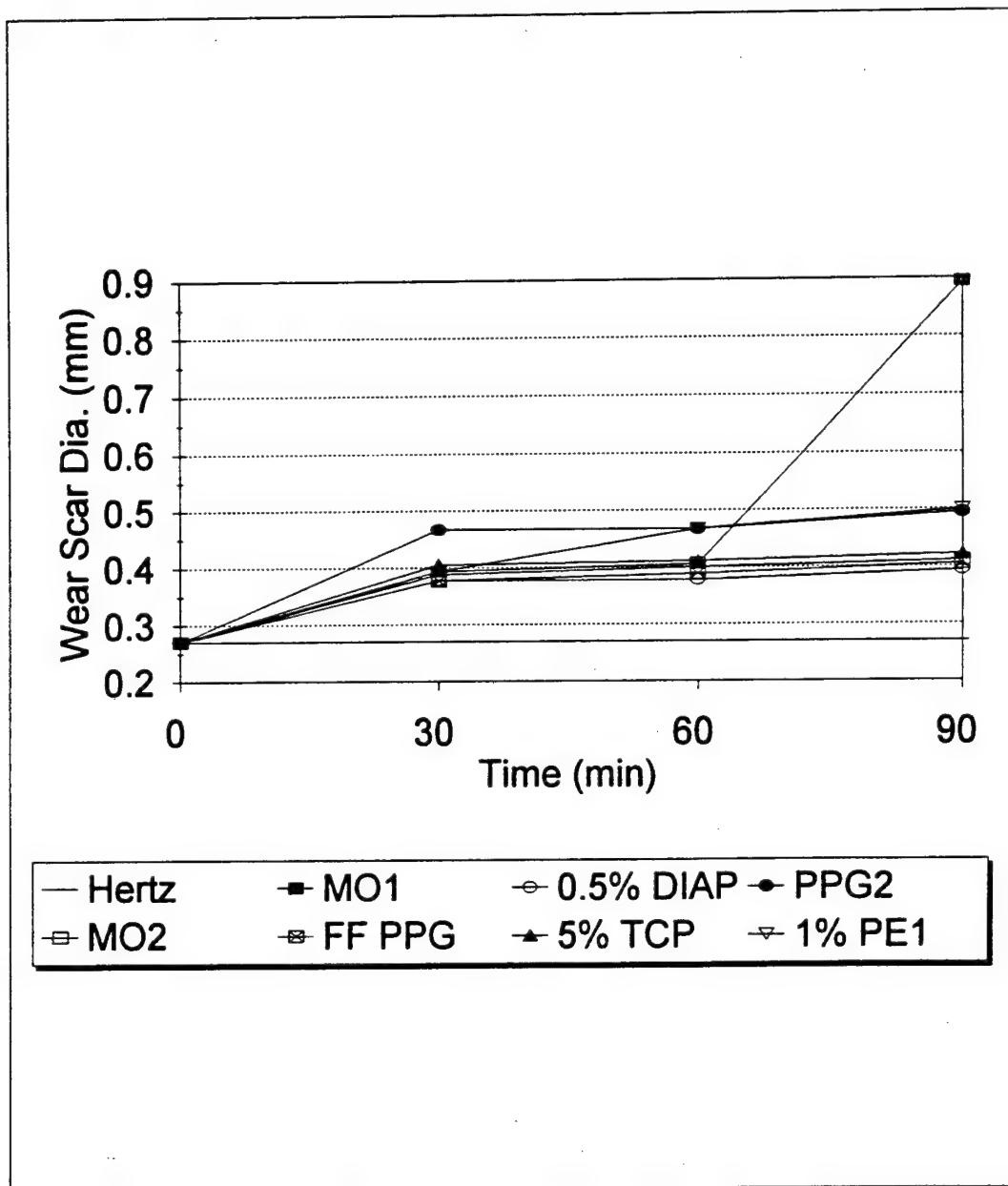
Continued testing was done by increasing the load in 2 kg intervals up to 10 kg total using PPG 2 with 5% DIAP. These tests were run for a total of 60 minutes. From these results shown in Figure 4.4, a load of 8 kg was chosen for further testing because this gave the largest delta scar without scuffing.

Data for the sequential testing at the 8 kg load is shown on Figure 4.5. Tests at this load eliminated the additive PE1 due to its larger wear scar over the first two runs than the current MO1. The remaining lubricants, other than the neat PPG2, were all very similar in scar diameter over the first two runs. Once again, the significant difference is on the third run with white oil. The wear rate of the current mineral oil increases severely while the wear rate of both 0.5% DIAP and 5 %TCP remain fairly constant. This means the DIAP and TCP additives in PPG2 are developing a film which protects the surface even after the lubricant has been removed. This result is similar to the steel on steel test already mentioned. The other mineral oil evaluated, MO2, was found to behave differently than MO1. MO2 was found to have additives which will protect the aluminum surface after the bulk MO2 is replaced with a white oil. The fully formulated polyalkylene glycol (FF PPG) provided wear protection nearly identical to the PPG2 with 0.5 % DIAP. Therefore, the antioxidant additives do not adversely affect the performance of DIAP on a steel on aluminum system.



Lubricant: PPG2 + 0.5% DIAP  
Material: Steel 52100 on Al 2618 T6  
Temperature: 75 C  
Speed: 600 rpm  
Time: 60 min

Figure 4.4 Several Loads of Ball on Three Flats with Steel on Aluminum



Materials: Steel 52100 on Al 2618 T6

Load: 8 kg  
Temperature: 75 C

Base Lubricant: PPG2  
Speed: 600 rpm

Figure 4.5 Sequential Ball on Three Flats for Steel on Aluminum at 8 kg

#### 4.4.2 B. Steel on NAB

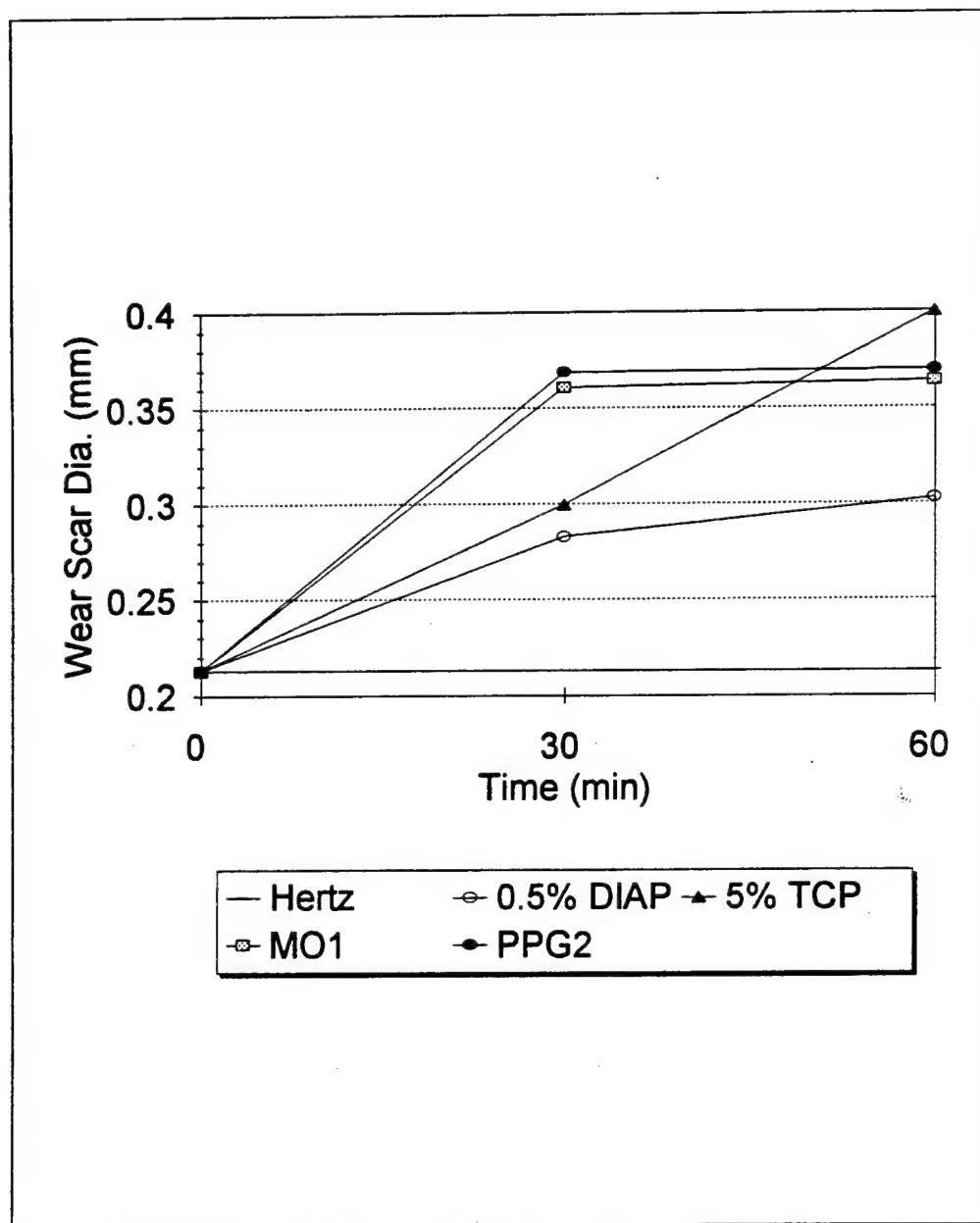
The steel on NAB system was tested using a continuous ball on three flats tests. The setup for this test is identical to the sequential ball and three flats test. The difference is that separate samples were run for periods of time of 30 and 60 minutes rather than one sample run with three consecutive 30 minute runs. The continuous test does not allow for testing of a protective film by using white oil. The continuous test was used because of difficulties in aligning the wear scar in the sequential testing mode.

The results from these tests are on Figure 4.6. It is clearly evident that the PPG2 with 0.5% DIAP is far superior to the MO1 and the other additives tested. The neat PPG2's performance was very similar to mineral oil. The 5% TCP appears to be corrosive on the NAB as indicated by the continually increasing wear scar.

#### 4.4.3 Pins on Ring Test

The pins on ring test was utilized to evaluate the lubricants performance under operating conditions that would be more similar to the actual system conditions than the four ball tests. This includes an intermittent spray of lubricant on the wear surface and also a steam environment.

Previous work had optimized the test conditions as specified earlier. The prior testing had tried continuous lubrication but the results showed the lubricant to be forming a hydrodynamic film which prevented an effective comparison between lubricants. The five second prelube proved to be the most effective lubricant application procedure to evaluate different lubricants. As described earlier, the "five second prelube" consists of a



Materials: Steel 52100 on NAB

Base Lubricant: PPG2  
Temperature: 75 C

Load: 5 kg  
Speed: 600 rpm

Figure 4.6 Continuous Ball on Three Flats for Steel on NAB

five second period during which oil is applied on the disk surface followed by a five second period without additional lubrication before the pins are worn for a one second time period. The ring is continuously spinning at 1995 rpm (13 m/s) during the five second prelube.

Testing on the pin on ring tester focused on three pin materials: Al 2618 T6, NAB, and C86300 (manganese bronze). The ring material was steel 387 for all tests. The temperature of the test was 260 °C and the environment of the wear chamber was steam also at 260 °C. The load on the pins was 600 psi.

Evaluation of wear rates are based on the volume of material lost per unit sliding distance. Previous work on a water soluble polyalkylene glycol based lubricant referred to as WS PAG is also included in the results. It is a fully formulated oil that previous work had eliminated as possible replacement lubricant based on severe levels of foaming when tested in the high speed water vortex of the actual operating system.

The results of the pin on ring tests are summarized in Table 4.9. The FF PPG lubricant shows slightly better performance than both MO1 and MO2 on the NAB. The WS PAG had a wear rate more than double that exhibited by FF PPG. Although the additive packages are not the same, the difference is more likely explained by the WS PAG being washed off the ring surface by the steam. This would leave less lubricant and additives to protect the surfaces. For C86300 on steel trials, the FF PPG again proved to show a slightly lower wear rate than MO1. This difference, however, is minimal.

The results of the aluminum on steel proved drastically different. The pins lubricated with the FF PPG showed a wear rate approximately forty times greater than the

Table 4.9 Pins on Ring Wear Data

Load: 600 psi (1 second pulses)  
 Speed: 1995 rpm  
 Temperature: 500 F (260 C)  
 Atmosphere: steam @ 500 F (260 C)

Lubricant	Material		Wear Rate (1.0e-06 cc/m)		
	Pin	Ring	Left Pin	Right Pin	Average
FF PPG	NAB	Steel ASTM 387	30.1	28.1	29.1
MO1	NAB	Steel ASTM 387	31.1	29.3	30.2
MO2	NAB	Steel ASTM 387	39.7	31.0	35.4
WS PAG	NAB	Steel ASTM 387	65.1	64.8	65.0
<hr/>					
FF PPG	AL 2618 T6	Steel ASTM 387	299	342	321
MO1	AL 2618 T6	Steel ASTM 387	7.4	8.0	7.7
MO2	AL 2618 T6	Steel ASTM 387	26.9	27.4	27.2
WS PAG	AL 2618 T6	Steel ASTM 387	408	368	388
<hr/>					
FF PPG	MnBronze	Steel ASTM 387	0.94	1.11	1.03
MO1	MnBronze	Steel ASTM 387	1.45	1.01	1.23

wear rate observed with MO1. The two mineral oils had relatively similar results as did the two polyalkylene glycols. This is in stark contrast to the ball on three flats data with the steel on aluminum. In the ball on three flats test, FF PPG protected the aluminum surface better than MO1. The two most significant differences between the pins on ring and the ball on three flats test are the temperature difference (260 °C versus 75 °C) and the 260 °C steam atmosphere in the pins on ring test.

The one major difference found while running the aluminum pins on ring tests was in the appearance of the pins. A thin black layer formed on the contact surface of the pins. The layer was not continuous but rather in several streaks in the direction of wear. The difference is with both mineral oils, the dark streaks usually lasted throughout the test. The FF PPG occasionally showed these dark streaks, but only during wear-in and they never lasted through a normal wear run once the chamber was heated and steam was added. Lubricant was applied during the wear-in period, but there was no steam in the chamber and the system was at room temperature.

The aluminum pins lubricated with FF PPG showed severe wear. Some of the aluminum pins appeared to have softened and flowed into a lip around the original diameter of the pin. This means the temperatures in the contact region must have approached the melting point of the Al 2618 T6. The melting point of most aluminum alloys is between 570 and 660 °C. With the mineral oils these high temperatures were apparently forming permanent aluminum oxide coatings which protected against wear. The tests with the FF PPG however did not maintain the oxide film. Instead the pins were quickly worn away. Oxidation testing that will be described later found the FF PPG

lubricant to volatilize much quicker than MO1. As a result of less lubricant remaining on the ring surface, the contact temperatures in the FF PPG testing may be higher than with MO1. One possible explanation is the thicker MO1 film is able to carry off enough excess heat to keep the temperature below the melting point of the aluminum. Another possibility is the thicker MO1 film is reducing friction and therefore less additional heat is generated with MO1.

The temperatures of the pin surface may be reaching higher temperatures than are actually seen in the operating system due to the inability of the pin to transfer heat efficiently away from the surface. Poor contact between the pin and the pin holder may be preventing adequate heat removal. In the actual system, the large aluminum piston would be able to transfer heat away from the surface and into its surroundings much more effectively. The different behavior of the polyalkylene glycol lubricants versus the mineral oil lubricants on the aluminum on steel pins on ring test is an area which needs further investigation to understand completely what is occurring.

In the actual operating system, the problem observed with the aluminum on steel 387 pins on ring test could be solved by covering the aluminum surfaces that are experiencing similar conditions with NAB plates. The NAB plates would significantly reduce the wear. This has been an option from the beginning and was the reason the NAB material was evaluated throughout the wear testing. The C86300 could also be considered as a material for wear plates.

#### 4.5 Oil Oxidation and Volatility Results

The Penn State Micro-Oxidation Test (PSMO) was used to evaluate the oxidative stability of the potential replacement lubricants. This test provides an evaluation of a lubricant's volatility, deposit forming tendency and molecular weight distribution after oxidation. A lubricant layer of approximately 180 microns thick is applied on a low carbon steel test cup as previously described. The thin lubricant film is chosen to minimize effects of oxygen diffusion into the lubricant. The PSMO has been described and utilized for several applications in a number of publications [53, 51, 52, 58, 59, 60, 61].

The MO1 mineral oil and the neat PPG2 were evaluated at 225 °C for 30 minutes. The results are shown on Table 4.10. The mineral oil clearly out performed PPG2 in both volatility and deposit formation under these conditions. Clearly the mineral oil evaporates at a significantly slower rate. After 30 minutes, the mineral oil also shows slightly less deposits than PPG2. However, PPG2 has reached its final deposit, meaning there is no liquid lubricant remaining to increase the amount of deposit. This "clean burn off" will help prevent circulating or lubricating problems which may develop with a large amount of deposits. The final deposit of the mineral oil was found to be over 55 weight percent. The low final deposit of the PPG2 is a significant advantage over the mineral oil.

A variety of oxidation inhibitors were added to the PPG2 to increase its oxidative stability. They were subjected to the same operating conditions as mentioned above for the neat fluids. The results of PPG2 with single additives are also shown on Table 4.10. The additive concentrations were determined from recommendations from the manufacturer when available. It is evident that increasing the amount of copper additive

**Table 4.10 Oxidation Testing—Neat Fluids and Additives**

Temperature: 225 C (437 F)

Time: 30 minutes

Air Flow Rate: 20 cc/min

Lubricant	% Evaporation	% Deposit	% HMW	% SMW	Total
MO1	8.82	1.31	—	—	
	3.42	2.04	—	—	
PPG2	97.98	1.64	0	0	99.6
	95.81	3.47	0	0	99.3
PPG2 + 0.5% DIAP	97.86	1.66	0	0	99.5
	97.69	1.87	0	0	99.6

**Oxidation Inhibitors In PPG2**

500 ppm Cu	88.26	2.15	2.2	10.9	103.5
1000 ppm Cu	81.09	0.96	5	18.8	105.9
	82.51	1.03	3.2	16.1	102.8
2000 ppm Cu	71.08	0.59	5.6	31.2	108.5
	72.59	1.69	4.2	27.0	105.5
0.5% TBP	96.85	2.70	—	—	99.6
0.5% DPA	96.36	3.39	—	—	99.8
1.0% PNA	95.76	3.23	—	—	99.0

improves the oxidative performance of the polyalkylene glycol. This is similar to studies on mineral oils, polyol esters and polyalphaolefins which also found increasing levels of oil soluble copper salts to improve the oxidation behavior of the lubricants [62, 63]. The addition of TBC, DPA and PNA in specified concentrations showed little effect in performance when compared to the neat fluid under the specified conditions.

Combinations the various oxidation additives were combined in an effort to maximize oxidative stability. For most of these tests, 0.5 weight percent DIAP was added since it was previously determined to be the most effective wear additive. The results of the combined additives in PPG2 are shown in Table 4.11. Once again, the combinations containing the Cu additive exhibit the best performance. The combination of 2000 ppm Cu and 0.5 weight percent TBC gave the best results. Addition of the DIAP wear additive had a negligible effect to the Cu-TBC additive package. The DIAP additive actually reduced the deposit when combined with PNA in the PPG2 base fluid.

Due to environmental concerns over the toxicity of copper additives over 100 ppm [64], the Cu antioxidant was eliminated as a possibility for this application. This left the antioxidant combination of PNA and TBC as the best choice. The 1.0 weight percent of both PNA and TBC along with 0.5 weight percent of DIAP was the only non-Cu containing additive combination which showed a residual amount of liquid after 30 minutes at 225 °C. The combination of the three additives will be referred to as "FF PPG" as previously mentioned. This combination also produced the least amount of deposit of those fluids tested. However, the difference between the neat PPG2 and the PPG2 fluid with DIAP, PNA and TBC was only 2-3 weight percent in evaporation and deposit at 30

Table 4.11 Oxidation Testing—Additive Combinations

Temperature: 225 C (437 F)

Time: 30 minutes

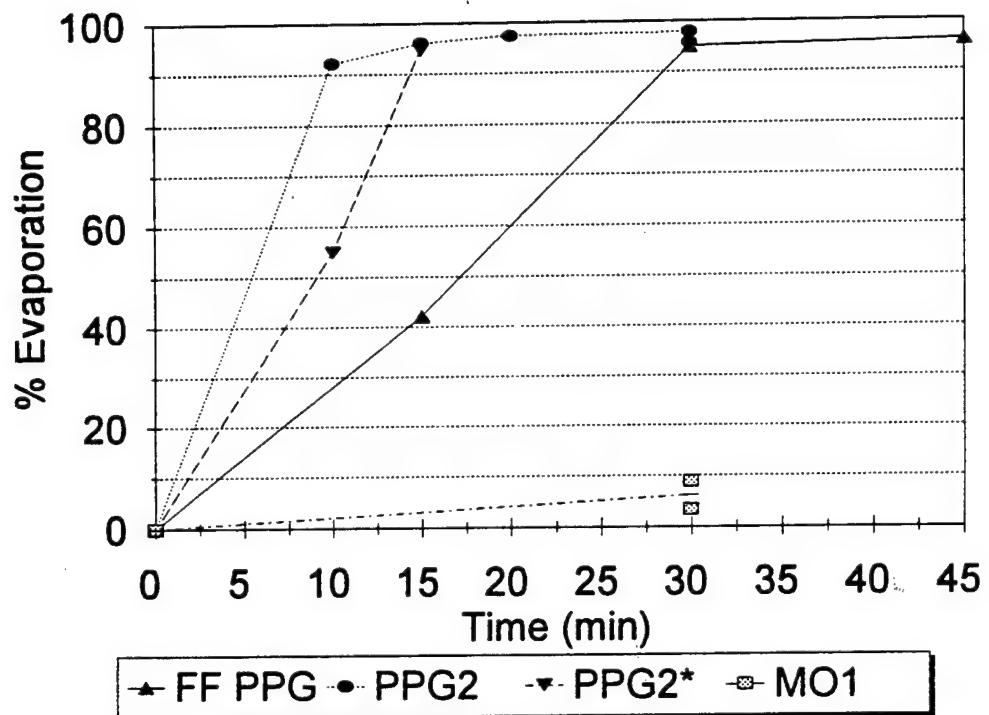
Air Flow Rate: 20 cc/min

Lubricant	% Evaporation	% Deposit	% HMW	% SMW	Total
<b>Additives in LB 625</b>					
2000 ppm Cu + 0.5% TBP	55.45	0.57	4.5	41.6	102.1
	47.41	0.56	5.8	50	103.8
500 ppm Cu + 0.5% DIAP + 0.5% TBP	89.38	0.45	--	--	
	89.52	0.09	3.2	10.9	103.7
1000 ppm Cu + 0.5% DIAP + 0.5% TBP	73.76	0.27	2.4	23.5	99.9
	55.47	0.46	6.3	33.3	95.5
1.0% PNA + 0.5% DIAP	97.04	1.05	* small amount		98.1
	97.02	0.93			98.0
0.5% DIAP + 1% PNA + 1.0% TBP	94.81	0.33	* small amount		95.1
	95.45	0.20			95.6

minutes.

In order to further evaluate the additive package in FF PPG, particularly in terms of evaporation/volatility, times of less than 30 minutes were tested at 225 °C on the PSMO test. The neat PPG2 along with additive packages containing both 0.5 and 1.0 weight percent antioxidants were evaluated. Figure 4.7 shows the results of these experiments. These results clearly show that the antioxidants at the 1.0 weight percent concentration slow evaporation and volatility significantly more than the lower concentration antioxidant and neat PPG2. Less volatility would result in more lubricant staying on the wear surfaces for longer periods of time. More lubricant remaining on the surface for longer periods of time would enhance wear protection.

The slowed volatility of FF PPG still does not approach the low levels of volatility of MO1. The actual operating system applies lubricant every time the piston moves forward so it is not essential for the lubricant to remain in the system for extended periods of time. For this reason, there was no attempt to match the low volatility of MO1. Also, the FF PPG still does not leave a deposit as was the case with the neat PPG2.



\* Contains: 0.5% DIAP + 0.5% PNA + 0.5% TBP

Temperature: 225 C (437 F0)  
Time: 30 minutes  
Air Flow Rate: 20 cc/min

Figure 4.7 Oxidation - Volatility Rate Testing

## Chapter 5

### GREASE RESULTS AND DISCUSSION

#### 5.1 Greases Evaluated

This research investigated commercial greases with mineral oil and polyalphaolefin (PAO) base fluids with either clay or lithium complex soap thickeners. A general description of the greases is given in Table 5.1. Several other grease were considered, but were eliminated early in the study based on preliminary wear results and the desire for extreme pressure (EP) properties and are therefore not reported here. All the greases except for the current grease (SYN A) contain EP additives. As mentioned earlier, this was an initial requirement of all replacement greases due to the increasing loads in the gear system.

The penetration range of the test greases was kept between  $1\frac{1}{2}$  and 2. The importance of the penetration number relies primarily in the ability to pump the grease with the current pumping system. The grade 2 greases could present a problem in this area since they are slightly harder than the grade  $1\frac{1}{2}$  grease. They were investigated based on a statement from the manufacturer saying that SYN C in particular would pump as a much softer grease. This is partially due to its synthetic base fluid. Also, the pumping system was not believed to be operating at its maximum capabilities.

In addition to the pumping benefits, a synthetic base fluid was preferred due to a potentially higher level of biodegradability. Continuing research will focus on finding an

Table 5.1 General Grease Description

	SYN A	MIN A	SYN B	SYN C
<b>Base Fluid</b>	PAO	mineral oil	PAO	PAO
<b>Thickener</b>	clay	lithium complex soap	lithium complex soap	lithium complex soap
<b>NLGI Grade</b>	1 ½	2	2	1 ½
<b>E.P. Properties</b>	no	yes	yes	yes
<b>Min. Dropping Point, (°C)</b>	232	232 +	246	246
<b>Base Oil Viscosity</b> cSt @ 40 °C cSt @ 100 °C	28.8 - 35.2 4 - 5 (ISO VG 32)	220 21	220 23.8	460 46.5

synthetic or vegetable based grease with high levels of biodegradability. Another benefit of polyalphaolefin based greases in particular is a longer usable life than mineral oil based greases. Kawamura [65] showed lithium greases with a polyalphaolefin (PAO) base fluid to have a longer usable life than a similar mineral oil based grease as measured by ASTM test method D 1741 and Federal Test Method 331.2. The PAO based grease lasted an average of approximately twice as long as the mineral oil based grease.

## **5.2 Grease Friction and Wear Test Results**

The friction and wear properties of the greases were evaluated using the standard four ball wear test and the extreme pressure four ball test. They were designed to evaluate the greases under the range of conditions they were likely to experience in the gear system. Actual data on the operating conditions was unavailable.

### **5.2.1 Standard Four Ball Test**

The procedure used was described previously and is similar to ASTM test method D 2266 [66]. The balls used in testing were steel 52100 balls. The top ball rotated at a speed of 600 rpm (23 cm/s). Evaluation of the greases was done over three temperatures: 28, 75 and 100 °C and at three loads: 40, 60 and 100 kg. This matrix of conditions was tested to cover the range of conditions predicted at lower loads. Focus was directed to the higher two temperatures since our system would operate primarily in that range.

A run time of 10 minutes was chosen for the majority of samples after testing under several conditions of load and temperature. After 10 minutes, the wear scars were

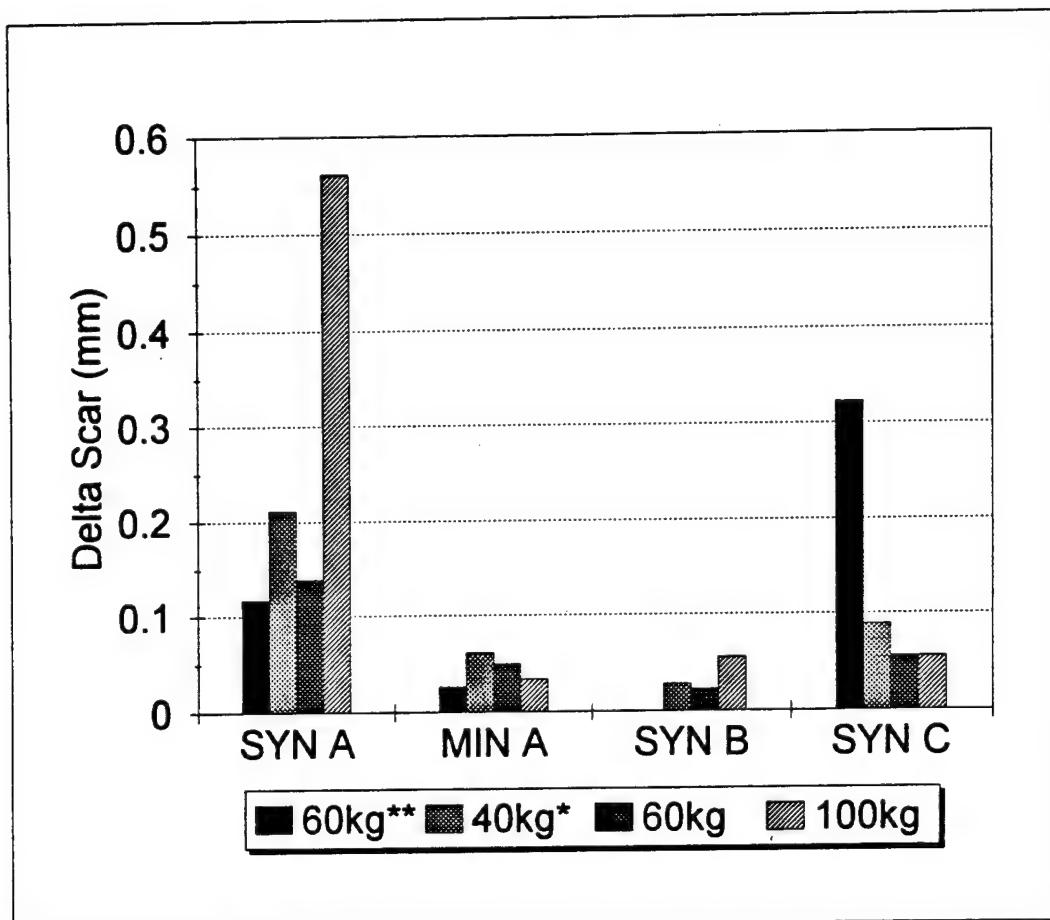
found to be the most repeatable primarily due to the grease staying in the contact area, especially under the higher loads. The lighter load of 40 kg was found to run for times of 60 minutes consistently similar to ASTM test method 2266. Longer run times were tested at the higher loads, but the results were not very repeatable due to the greases leaving the contact area more frequently. This was evidenced by a sharp increase in the friction plot and lead to a sharp increase in the wear scar diameter of the balls.

SYN C exemplifies the difference from maintaining grease in the contact area compared to a breakdown of the grease film. This is shown on Table 5.2 for only a 10 minute run time at the 100 kg load. The table clearly shows that the first and fifth run had drastically lower wear scars due to the grease remaining in the contact area and providing the lubricating film. Once the grease has been removed, there is nothing to prevent wear of the balls unless the additives can protect the surfaces until more grease is dragged into the contact area. The additive and soap film need to be continually replaced in order to maintain the optimum level of protection. It is apparent that in the four ball system, SYN C is not effectively replaced in the contact area. The shorter run time of ten minutes was able to minimize the occurrence of this large wear difference, but did not completely eliminate it. Higher temperatures were more likely to experience the this large increase in wear due to the loss of protective film. Subsequent values reported are those where grease has remained in the contact area, unless several attempts were unable to achieve this. Grease should be replaced in the contact area of the actual system as a result of the continual pumping of additional grease.

A summary of the standard four ball data is shown on Figures 5.1 and 5.2 for

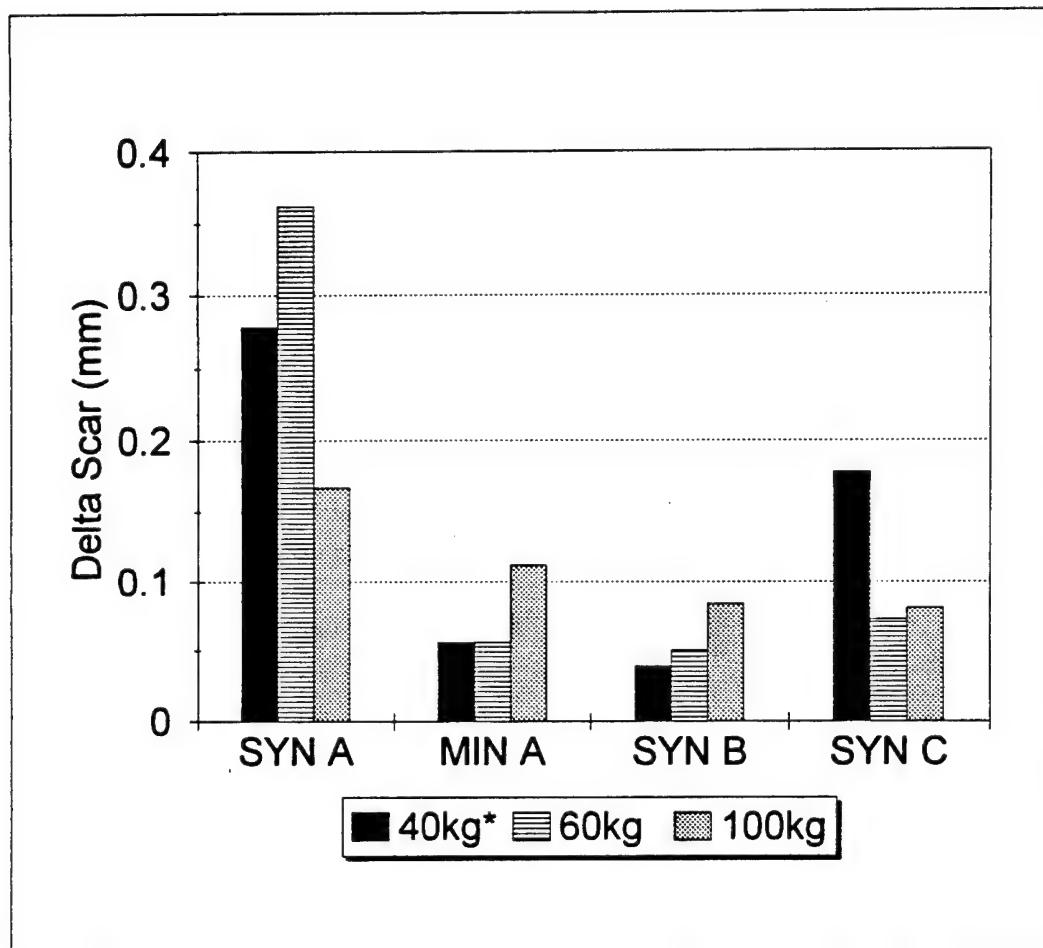
**Table 5.2** Maintaining Grease in the Contact Area

<b>Grease</b>	<b>Load (kg)</b>	<b>Time (min)</b>	<b>Temperature (C)</b>	<b>Delta Scars (mm)</b>
SYN C	100	10	100	0.095
				0.395
				0.401
				0.439
				0.067
				0.373



Time: 10 minutes (\* 60 min.)  
Speed: 600 rpm  
Temperature: 75 C (\*\*28 C)

Figure 5.1 Standard Grease Four Ball Data (75 C)



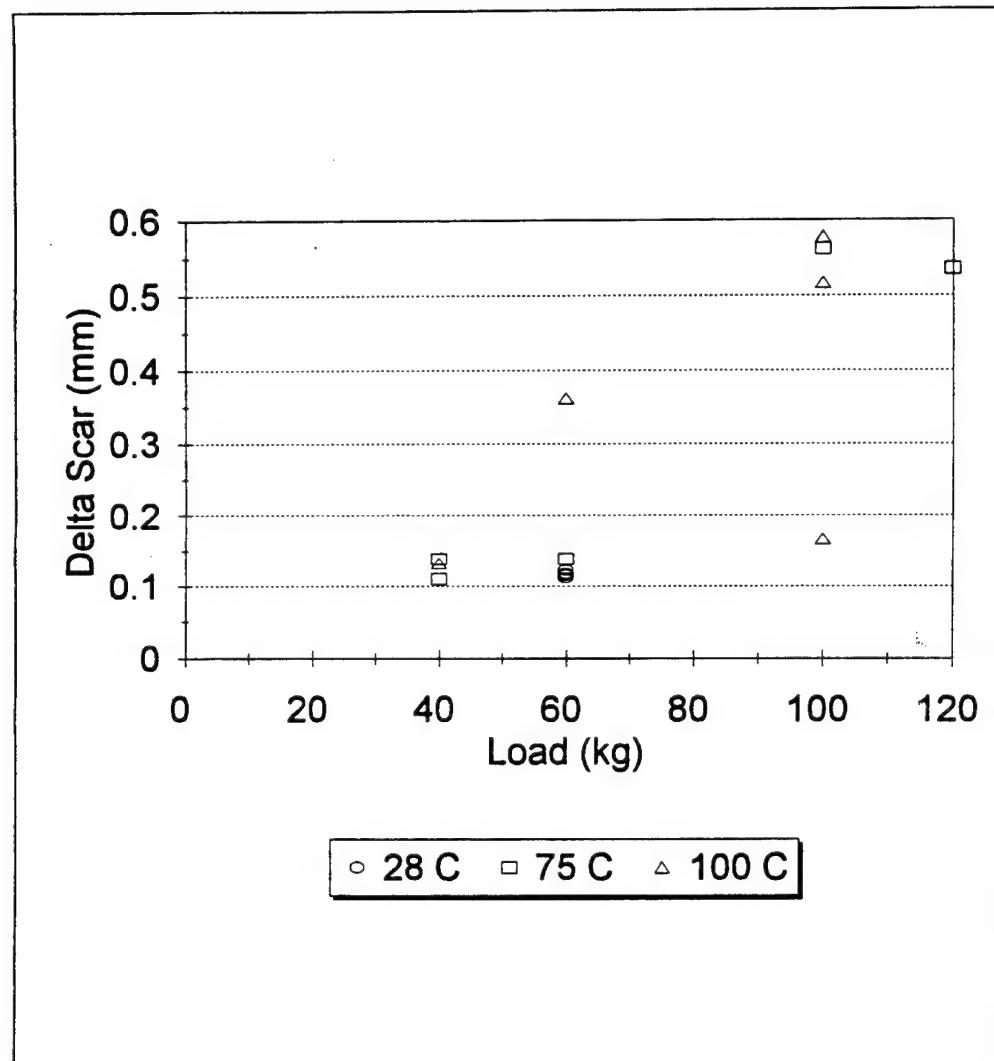
Time: 10 minutes (\* 60 min.)  
Speed: 600 rpm  
Temperature: 100 C

Figure 5.2 Standard Grease Four Ball Data (100 C)

temperatures of 75 °C and 100 °C respectively. It is readily evident that the current grease SYN A provides significantly less protection against wear than the proposed replacements. Even under the lowest load where the EP additives should not play a significant role in wear protection, SYN A shows significant wear. The individual four ball data of SYN A is displayed on Figure 5.3. There is a sharp jump in the delta wear scar between 60 and 100 kg. This is a result of exceeding SYN A's wear protection limit. Extreme Pressure testing will examine this range of loads closer.

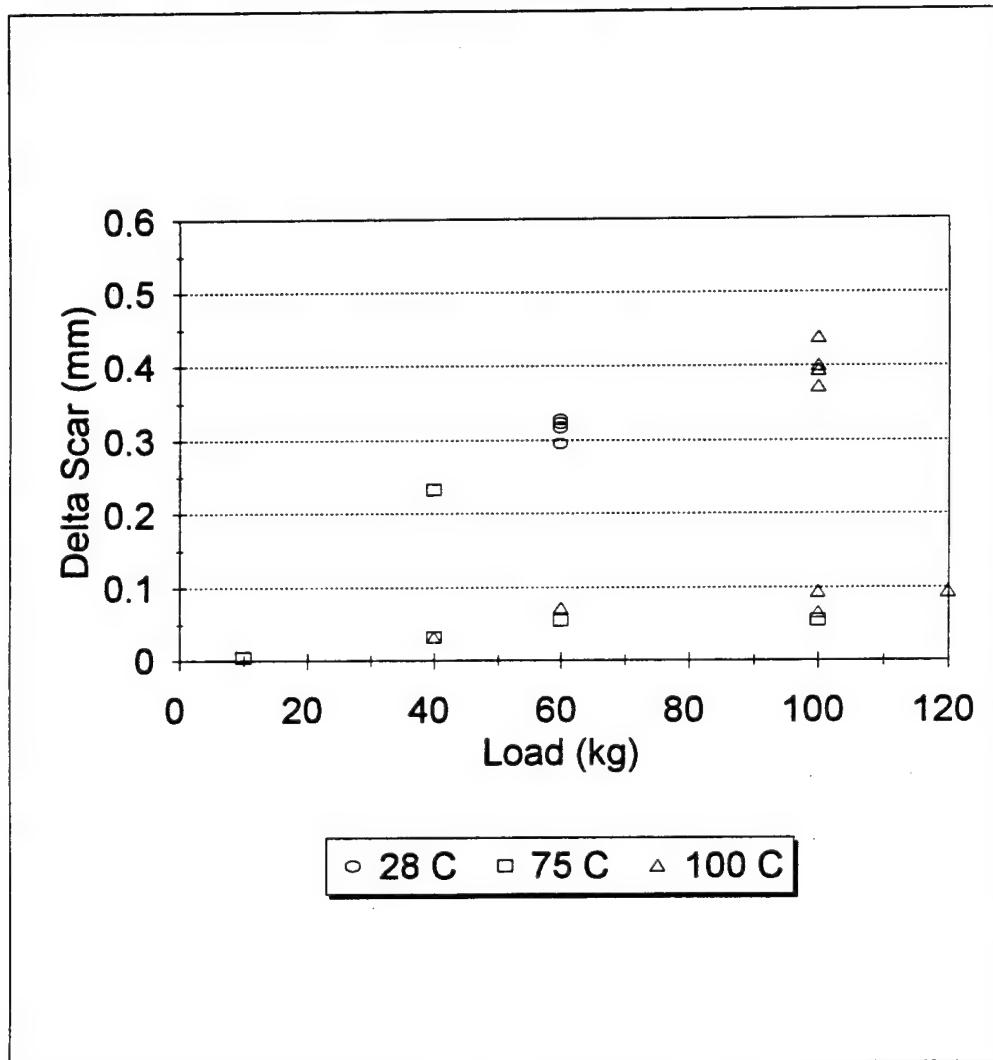
SYN A and SYN C were the only two greases tested which have a NLGI hardness of  $1\frac{1}{2}$ . SYN C also shows significant wear under certain conditions, particularly at the low temperature. This indicates the additives are not effective at lower temperatures. Higher temperatures and heavier loads are needed to activate the additives. At the conditions of 100 kg and 100 °C, SYN C was only able to protect the contact surface effectively two out of six times. SYN B and MIN A did not have this problem nearly as often. This may be a function of the softer grease having less thickener than the grade 2 greases. The four ball wear performance of SYN C is shown separately on Figure 5.4.

The NLGI grade 2 greases, SYN B and MIN A, showed consistently lower levels of wear than the softer two greases. The individual four ball wear results are shown on Figures 5.5 and 5.6 for SYN B AND MIN A respectively. There were seldom, if ever, cases of significant wear differences as mentioned previously with the softer greases. This may result from the harder greases being able to remain in the loaded contact area longer than the softer greases. Also, the additional soap thickener in the harder greases is helping to protect the surfaces. Studies by Horth showed that additional soap thickeners increase



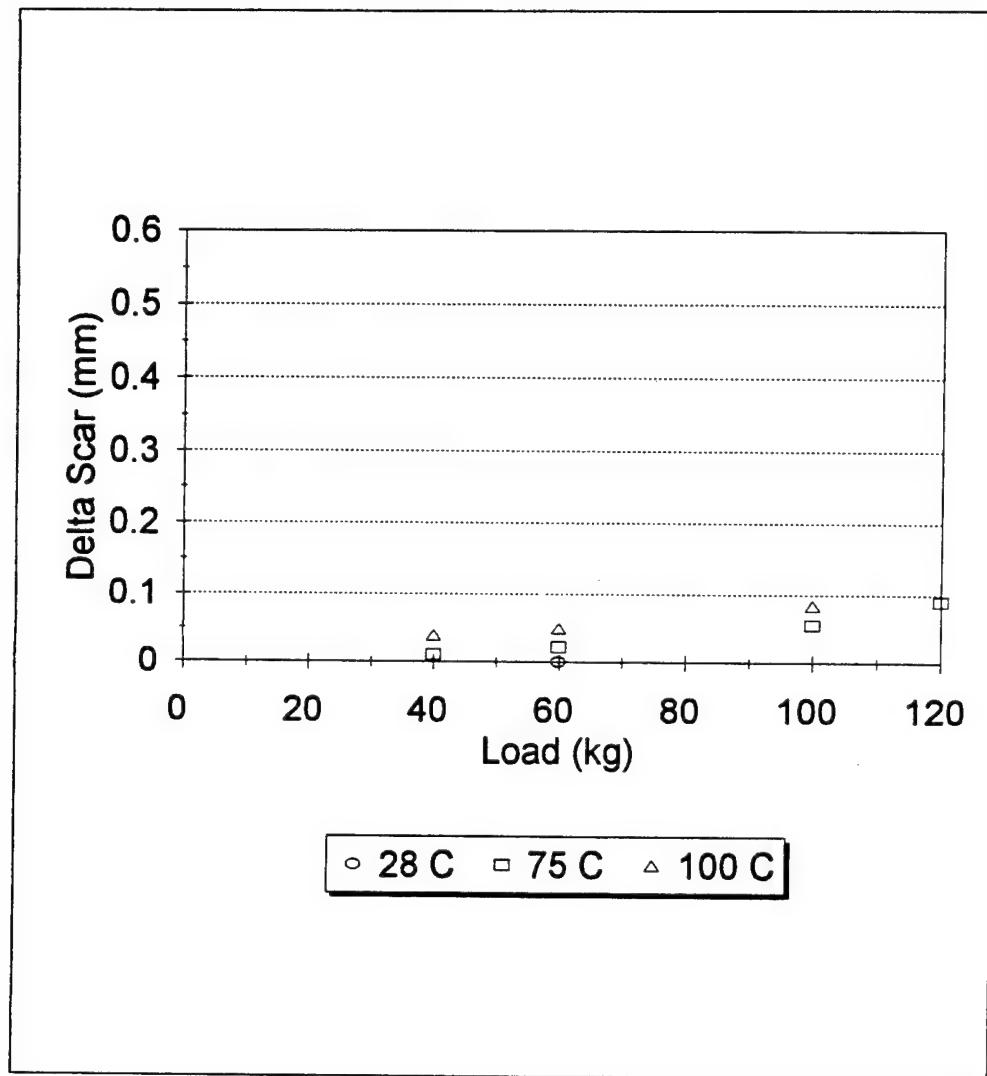
Speed: 600 rpm  
Time: 10 minutes

Figure 5.3 SYN A Four Ball Data



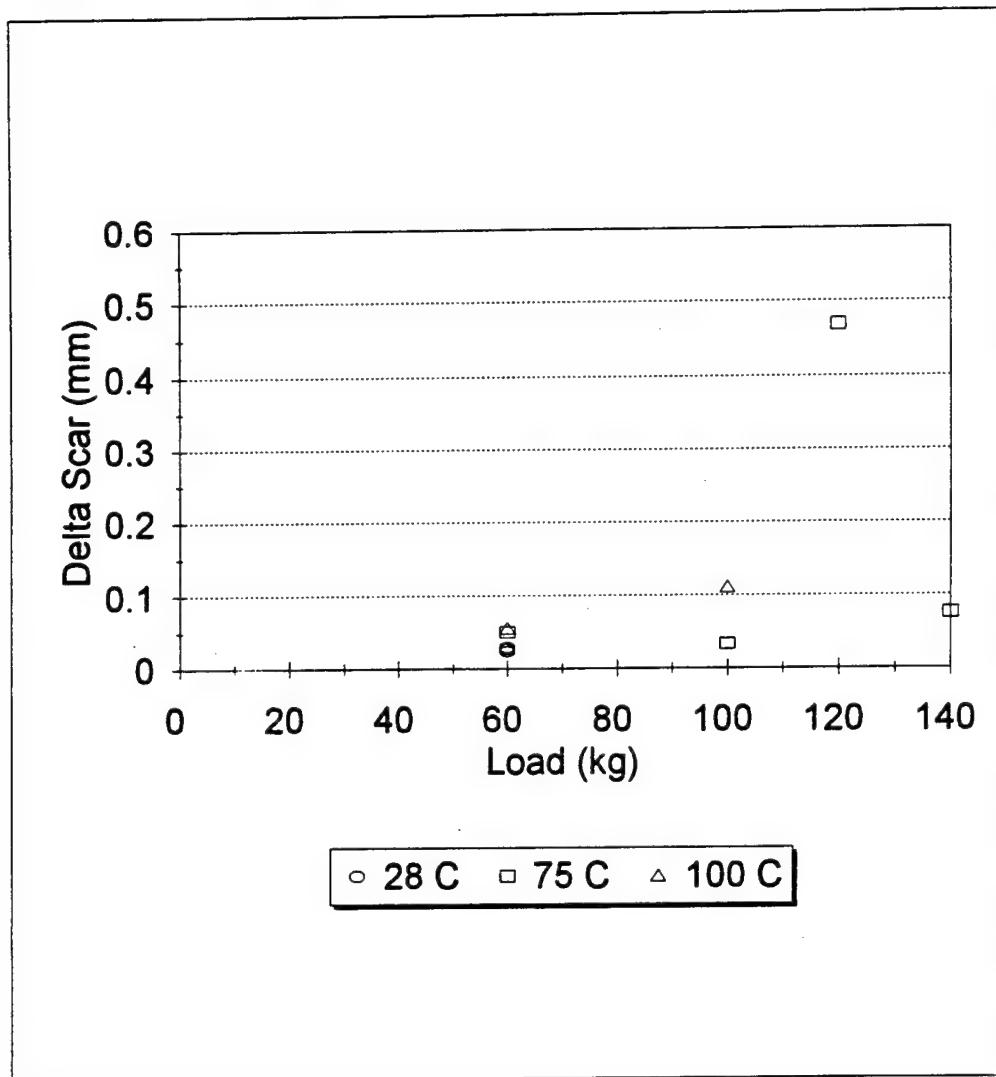
Speed: 600 rpm  
Time: 10 minutes

Figure 5.4 SYN C Four Ball Data



Speed: 600 rpm  
Time: 10 minutes

Figure 5.5 SYN B Four Ball Data



Speed: 600 rpm  
Time: 10 minutes

Figure 5.6 MIN A Four Ball Data

the boundary lubrication properties of greases [40]. There is not a clear trend between the PAO or mineral oil as base fluids in regard to wear protection.

### 5.2.2 Extreme Pressure Four Ball Results

Grease samples were tested under high loads with an extreme pressure (EP) four ball wear tester. The tests were done according to ASTM test method D-2596 [46]. This includes a sample volume of 10 ml, temperature of 27 °C, run time of 10 seconds and speed of 1760 rpm (68 cm/s). This test was meant to provide insight into how the greases will perform under the increasing loads being experienced in the gear system.

The results of the EP four ball test are shown on Table 5.3. The lack of EP additives in SYN A is clearly evident in the results. It shows significantly less protection than the other greases tested. The LNSL of 80 kg explains the sharp jump in the wear scar seen in the standard four ball testing. On the EP four ball test the lubricating film is beginning to break down at 80 kg. This helps explain the insufficient level of wear protection in the gear system with the increased loads being applied to the gears.

All three replacement greases show a marked increase in the Load Wear Index (LWI). The increased LWI will help to minimize the wear on the gears at the increased loads currently being seen in the gear system. The increased LNSL for SYN B and SYN C shows those greases further ability to provide increased protection under severe wear conditions. The increased weld point of the replacement grease candidates provides additional evidence of the effectiveness of the EP additives used in SYN B, SYN C and MIN A. The combined results from the EP testing indicate that all three replacement

**Table 5.3 Grease Extreme Pressure Four Ball Data**

Speed (rpm): 1760  
Temperature (C): 27  
Run Time (s): 10  
Ball Material: Steel 52100

	<b>Last Non-Seizure Load (kg)</b>	<b>Weld Point (kg)</b>	<b>Load Wear Index</b>
<b>SYN A</b>	80	200	36.1
<b>MIN A</b>	80	250* / 315	46* / 44.3
<b>SYN B</b>	---	250 *	45 *
<b>SYN C</b>	126	250* / 315	49* / 55.8

\* Manufacturer's reported value

greases would outperform the current SYN A grease under extreme conditions.

### 5.2.3 Friction Testing

Coinciding with this research on finding an improved grease was a project to redesign the bearings in the system. The goal of both projects was to increase the lifetime of the system. In order to properly model both the old and new versions of the operating system, friction data over a range of temperatures and loads was needed for any potential greases. To fulfill this requirement, friction testing was done on SYN B and SYN C over a range of temperatures and loads on the four ball wear tester. The conditions of testing were temperatures of 100, 150 and 200 °C with loads of 20, 40 and 60 kg at speeds of 600, 1200 and 1800 rpm (23, 46 and 69 cm/s respectively). The time was adjusted to maintain an equal sliding distance of 138 meters for all the tests. This correlates to a run time of 10 minutes at a speed of 600 rpm. The wear materials were all steel 52100 balls.

Both initial and final friction coefficients were determined. The initial friction coefficient was measured approximately one minute into testing. The final friction coefficient was determined from the last minute of testing. The repeatability of both the initial and final friction coefficient was determined by running six identical trials with SYN B. The conditions of testing were a 40 kg load, temperature of 100 °C and a top ball speed of 1200 rpm. The results are shown on Tables 5.4 and 5.5 for the initial and final coefficient respectively. The initial coefficient was found to be more consistent. Based on this result, the initial friction coefficient was used for the majority of analysis. Any inconsistencies obtained from the protective film breaking down occasionally during the

**Table 5.4 Repeatability of Initial Friction Coefficients**

Grease: SYN B  
Load: 40 kg  
Temperature: 100 °C  
Speed: 1200 rpm

Initial Friction Coefficient Data	Statistics	
0.056	mean	0.055
0.061	standard variation	0.00512
0.052	variance	$2.627 \times 10^{-5}$
0.050	minimum	0.049
0.049	maximum	0.061
0.060	confidence interval (95%)	0.00410

**Table 5.5 Repeatability of Final Friction Coefficients**

Grease: SYN B  
Load: 40 kg  
Temperature: 100 °C  
Speed: 1200 rpm

<b>Final Friction Coefficient Data</b>	
	0.051
	0.049
	0.055
	0.050
	0.065
	0.060

<b>Statistics</b>	
mean	0.055
standard variation	0.00636
variance	$4.040 \times 10^{-5}$
minimum	0.049
maximum	0.065
confidence interval (95%)	0.00509

middle of the test are minimized by measuring the friction early in the run. An additional advantage is the average contact pressures are more uniform from trial to trial earlier in the test. All tests at a given load begin with the same Hertzian pressure which decreases during testing as a result of wear. However, scar sizes and therefore contact pressures may vary at the end of the test. This is particularly true when comparing a poor lubricant to an excellent one. Recording the friction coefficient early in the run will minimize this difference in contact pressures.

A summary of the friction results is shown on Tables 5.6 and 5.7 for SYN B and on Tables 5.8 and 5.9 for SYN C. An overall statistical analysis of the combined initial and final friction coefficient for both greases is shown on Table 5.10. The overall average friction coefficient for SYN C is lower than the overall coefficient obtained from SYN B. The range of SYN C is larger due to friction coefficient values as low as 0.018. Little should be determined from this table other than a general impression of the two greases overall performance. Following figures will examine the friction coefficients of both greases in greater detail.

Graphs of the initial friction coefficients versus temperature are displayed on Figures 5.7 and 5.8 for SYN B and SYN C respectively for a speed of 600 rpm. Overall there is a slight decrease in the friction coefficient as temperature increases for both greases. This relationship was exemplary for most of the data collected under all operating conditions. Since there is only a slight temperature effect on the friction coefficient and this difference was relatively consistent, the remaining friction analysis combines all temperatures into one graph. This allows for a more general overview of the

Table 5.6 SYN B Initial Friction Coefficient

Sliding Distance: 138.2 m

Material: steel 52100

Speed: 600 rpm

		Temperature (C)		
		100	150	200
Load (kg)	20	0.072	0.065	0.060
	40	0.067	0.074	0.057
	60	0.067	0.066	0.059

Speed: 1200 rpm

		Temperature (C)		
		100	150	200
Load (kg)	20	0.060	0.048	0.046
	40	0.055	0.052	0.053
	60	0.057	0.063	0.059

Speed: 1800 rpm

		Temperature (C)		
		100	150	200
Load (kg)	20	0.036	0.044	0.030
	40	0.050	0.056	0.038
	60	0.057	0.054	0.049

Table 5.7 SYN B Final Friction Coefficient

Sliding Distance: 138.2 m  
 Material: steel 52100

**Speed: 600 rpm**

		100	150	200
		0.073	0.066	0.060
Load (kg)	20	0.065	0.068	0.052
	40	0.065	0.065	0.058
	60	0.065	0.065	0.058

**Speed: 1200 rpm**

		100	150	200
		0.060	0.051	0.048
Load (kg)	20	0.052	0.051	0.048
	40	0.052	0.060	0.066
	60	0.052	0.060	0.066

**Speed: 1800 rpm**

		100	150	200
		0.045	0.044	0.032
Load (kg)	20	0.050	0.055	0.039
	40	0.060	0.054	0.052
	60	0.060	0.054	0.052

Table 5.8 SYN C Initial Friction Coefficient

Sliding Distance: 138.2 m

Material: steel 52100

Speed: 600 rpm

Temperature (C)

	100	150	200
20	0.046	0.040	0.044
40	0.062	0.057	0.059
60	0.071	0.065	0.060

Speed: 1200 rpm

Temperature (C)

	100	150	200
20	0.036	0.031	0.028
40	0.047	0.052	0.038
60	0.050	0.051	0.043

Speed: 1800 rpm

Temperature (C)

	100	150	200
20	0.029	0.019	0.025
40	0.037	0.036	0.033
60	0.041	0.043	0.040

Table 5.9 SYN C Final Friction Coefficient

Sliding Distance: 138.2 m

Material: steel 52100

Speed: 600 rpm

		Temperature (C)		
		100	150	200
Load (kg)	20	0.046	0.038	0.041
	40	0.064	0.058	0.070
	60	0.071	0.069	0.078

Speed: 1200 rpm

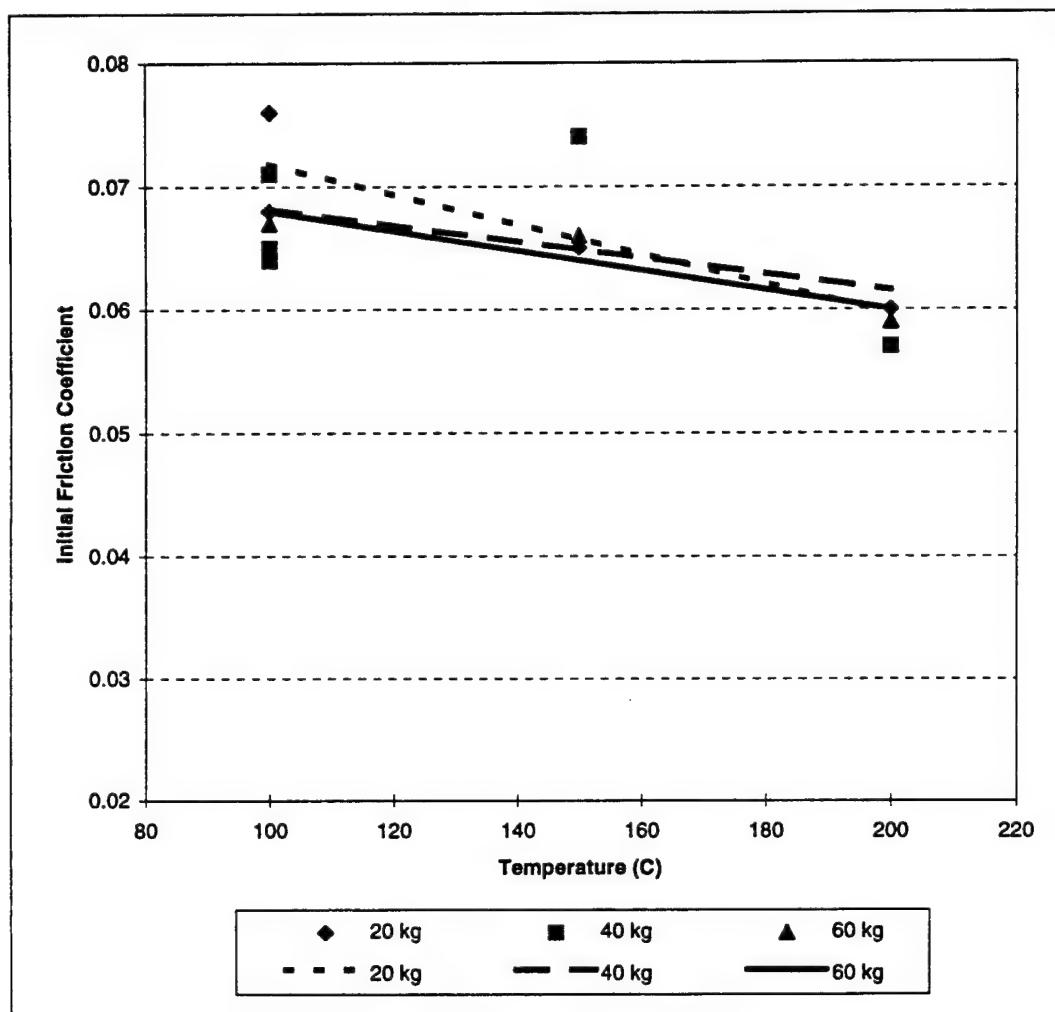
		Temperature (C)		
		100	150	200
Load (kg)	20	0.040	0.052	0.029
	40	0.050	0.052	0.053
	60	0.051	0.065	---

Speed: 1800 rpm

		Temperature (C)		
		100	150	200
Load (kg)	20	0.027	0.018	0.024
	40	0.054	0.051	0.043
	60	0.041	0.070	---

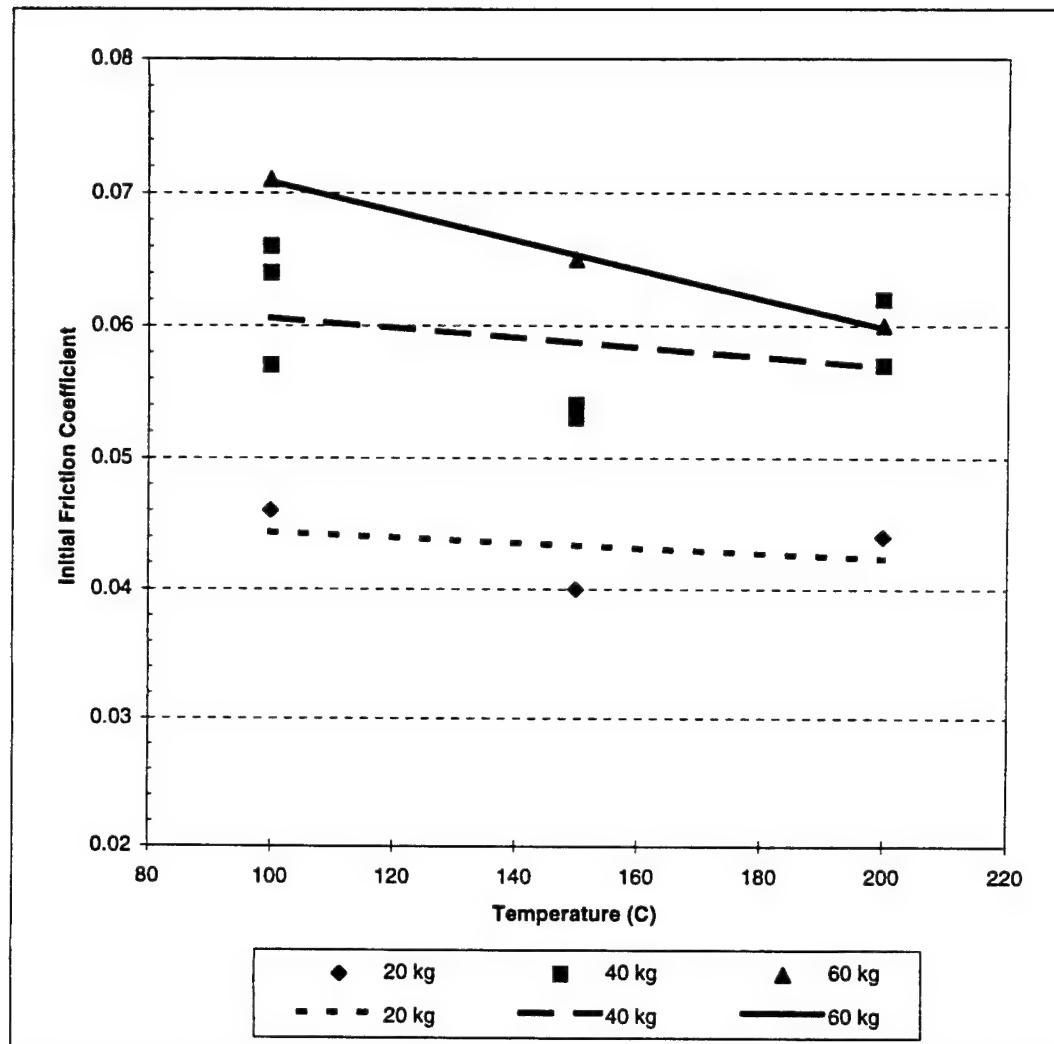
**Table 5.10 Overall Statistical Analysis of Initial and Final Friction Coefficients For SYN B and SYN C**

<b>Statistics</b>	<b>SYN B</b>	<b>SYN C</b>
mean	0.056	0.049
median	0.056	0.050
standard deviation	0.0101	0.0143
variance	$1.01 \times 10^{-4}$	$2.04 \times 10^{-4}$
range	0.049	0.060
minimum	0.030	0.018
maximum	0.079	0.078
confidence interval (95%)	0.00236	0.00354



Speed: 600 rpm  
Time: 10 minutes

Figure 5.7 SYN B Initial Friction Coefficient Versus Temperature



Speed: 600 rpm  
Time: 10 minutes

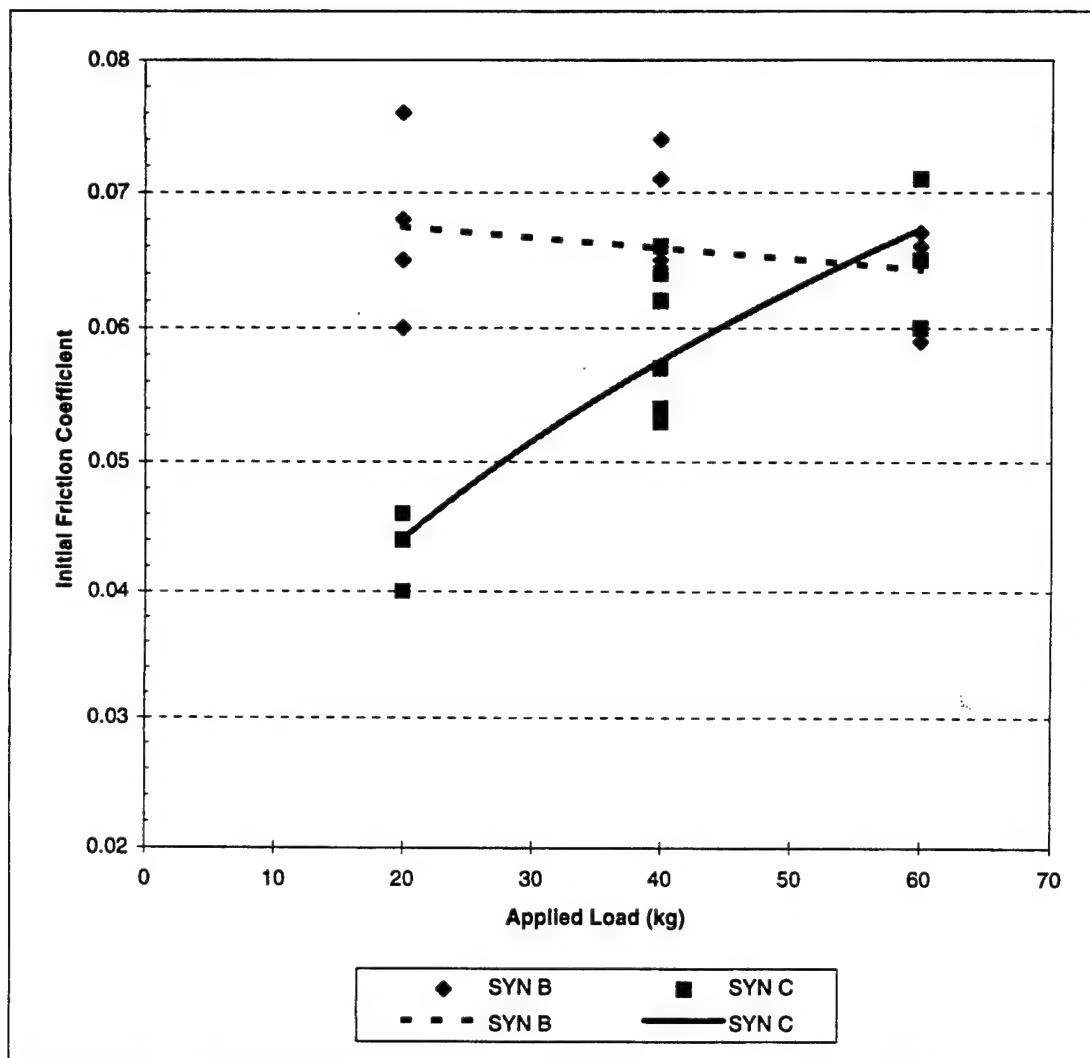
Figure 5.8 SYN C Initial Friction Coefficient Versus Temperature

trend in the friction coefficient.

One explanation for the slight decrease in the friction coefficient with temperature is that at 200 °C both SYN B and SYN C are approaching their dropping point. Under the high shear conditions of the four ball test, some of the base oil would begin to separate from the grease structure. The oil is able to flow through the contact area easily where the grease is unable to effectively flow. The extra oil in the contact area would help to protect the surfaces by building a protective film layer. This reduces the friction coefficient.

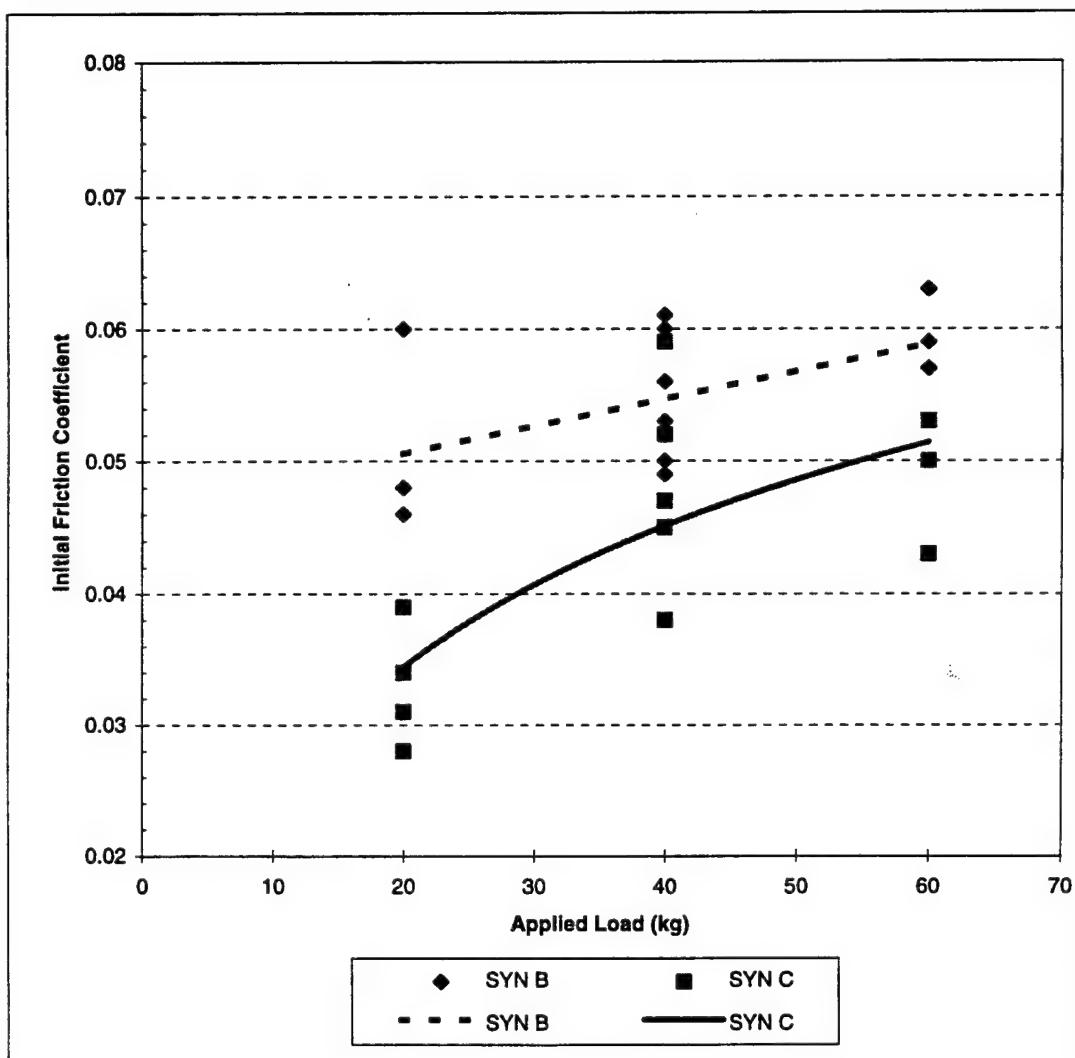
One difference that is evident under the conditions described in Figures 5.7 and 5.8 is that the friction coefficient of SYN B does not vary much with load. SYN C shows a wider spread in the trend lines at different loads. The effect of load on the initial friction coefficient is evaluated further in Figures 5.9 for the rotating speed of 600 rpm. It is apparent that the friction coefficient of SYN B tends to decrease slightly with increasing loads. SYN C, on the other hand, shows a significant increase in the friction coefficient with increasing loads.

The relationship between initial friction coefficient and applied load was examined for speeds of 1200 and 1800 rpm in Figures 5.10 and 5.11. It was found that at 1200 rpm the friction coefficient for SYN B now increases slightly with increasing loads. For 1800 rpm, the slope has increased even more. At this speed, the friction coefficient trend of SYN B nearly duplicates the friction coefficient trend of SYN C, only SYN B has a coefficient approximately 0.01 higher than SYN C. The trend is friction coefficient data for SYN C proved fairly constant with a gradual overall decrease of the coefficient with increasing speeds.



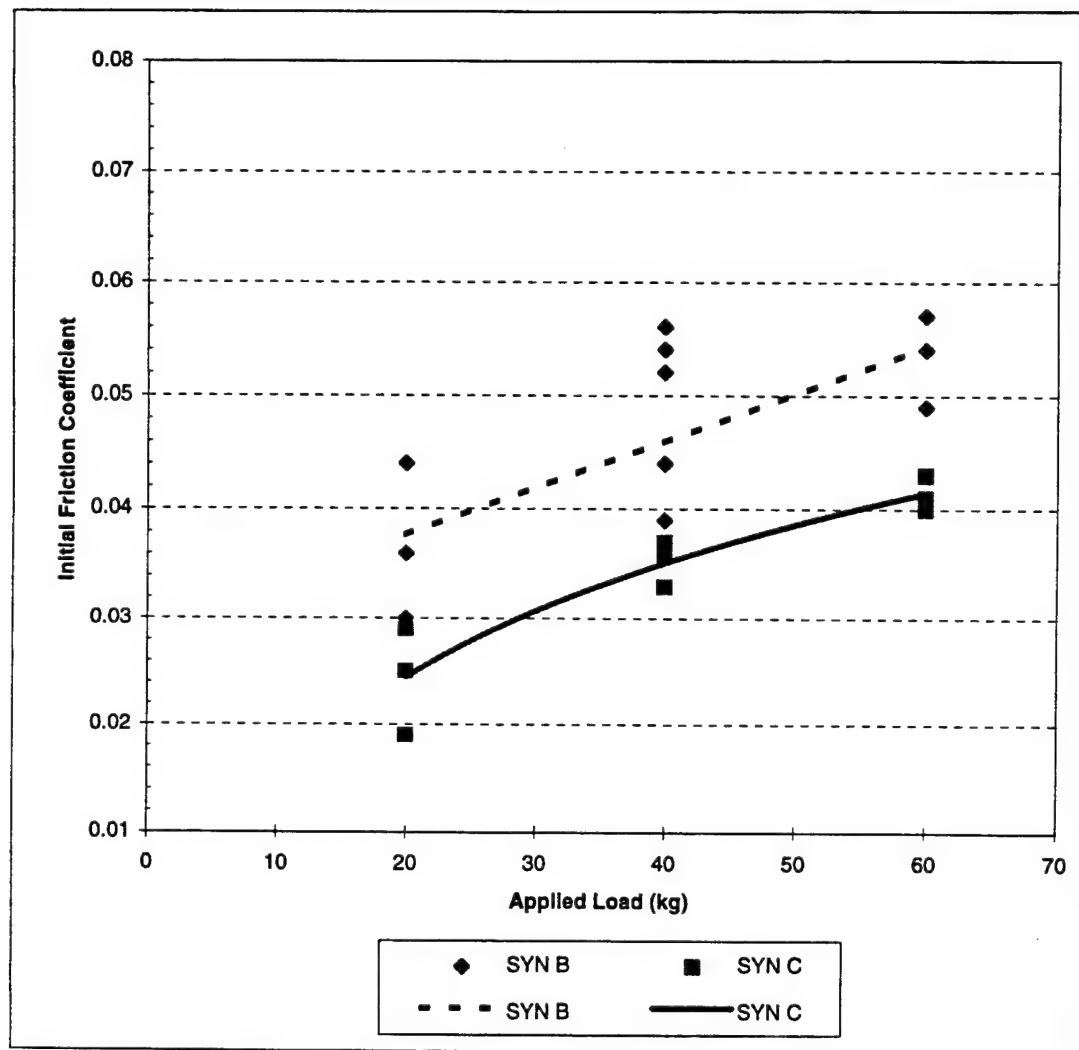
Temperature: 100, 150 and 200 C  
Speed: 600 rpm  
Time: 10 minutes

Figure 5.9 Initial Friction Coefficient Versus Applied Load (600 rpm)



Temperature: 100, 150 and 200 C  
Speed: 1200 rpm  
Time: 5 minutes

Figure 5.10 Initial Friction Coefficient Versus Applied Load (1200 rpm)



Temperature: 100, 150 and 200 C  
Speed: 1800 rpm  
Time: 3.3 minutes

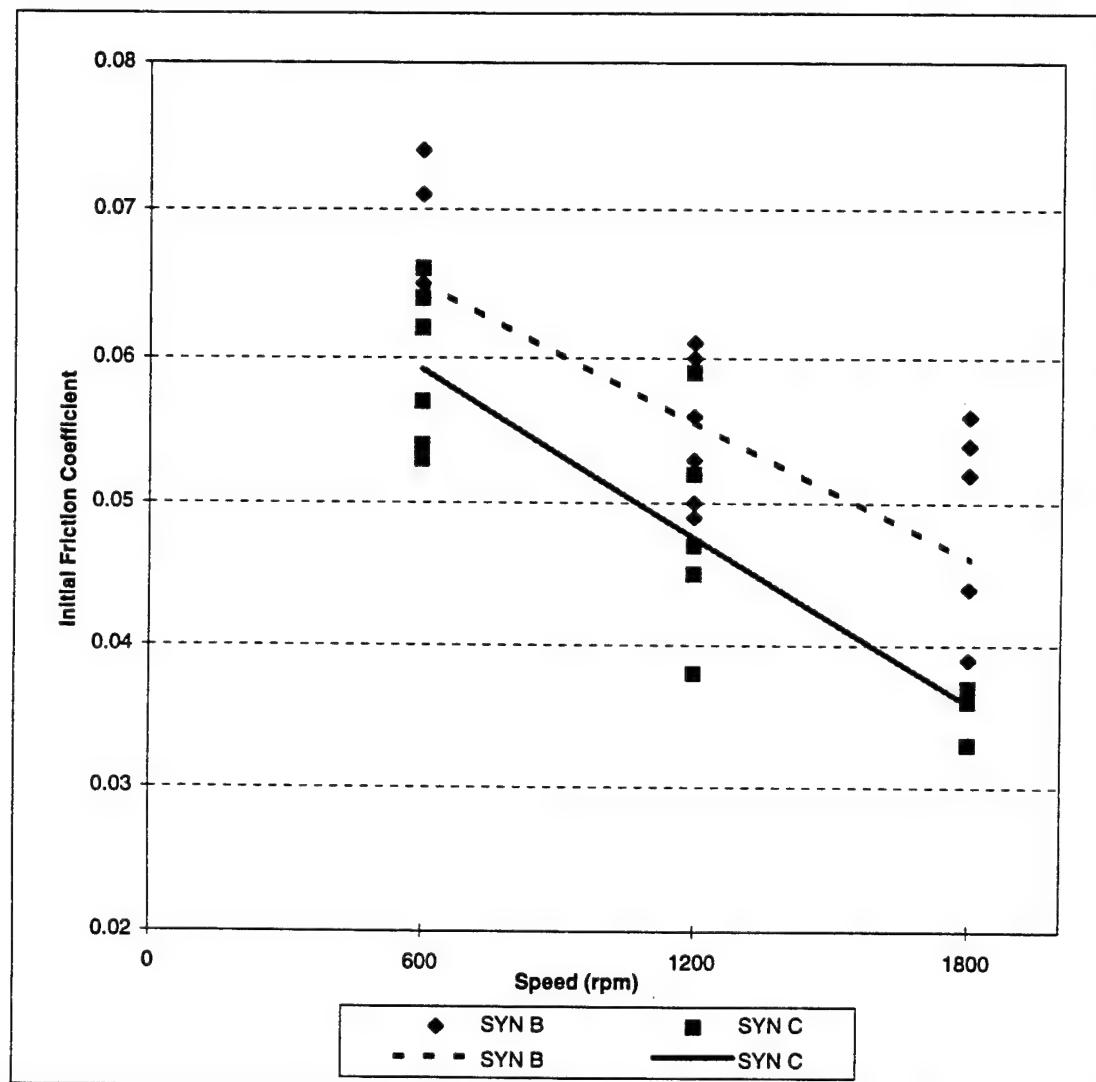
Figure 5.11 Initial Friction Coefficient Versus Applied Load (1800 rpm)

A consistent trend found throughout the friction testing was a general decrease in the friction coefficient with increasing rotation speeds. This is illustrated in Figure 5.12 for an applied load of 40 kg. Both greases shows a consistent decrease in friction with SYN C generally having a lower value than SYN B.

A comparison of the current grease, SYN A, with SYN B and SYN C was done at 100 °C at 1200 rpm. The results are shown on Figure 5.13. SYN A was found to have a friction coefficient between SYN B and SYN C at the 20 and 40 kg loads. However, at the 60 kg load, SYN A produced the highest friction coefficient. The cause of this increased friction results from the lack of an extreme pressure additive in SYN A. The EP four ball test showed that SYN A was no longer an effective lubricant at 80 kg based on the LNSL. The 60 kg load used in the friction testing is approaching this value and the wear protection is decreasing. The friction coefficient increases with increasing levels of wear. As the load increases to 80 kg a sharp jump in friction is expected indicating protective film failure. SYN B and SYN C should not see this sharp jump in friction until well over 100 kg based on their last non-seizure load.

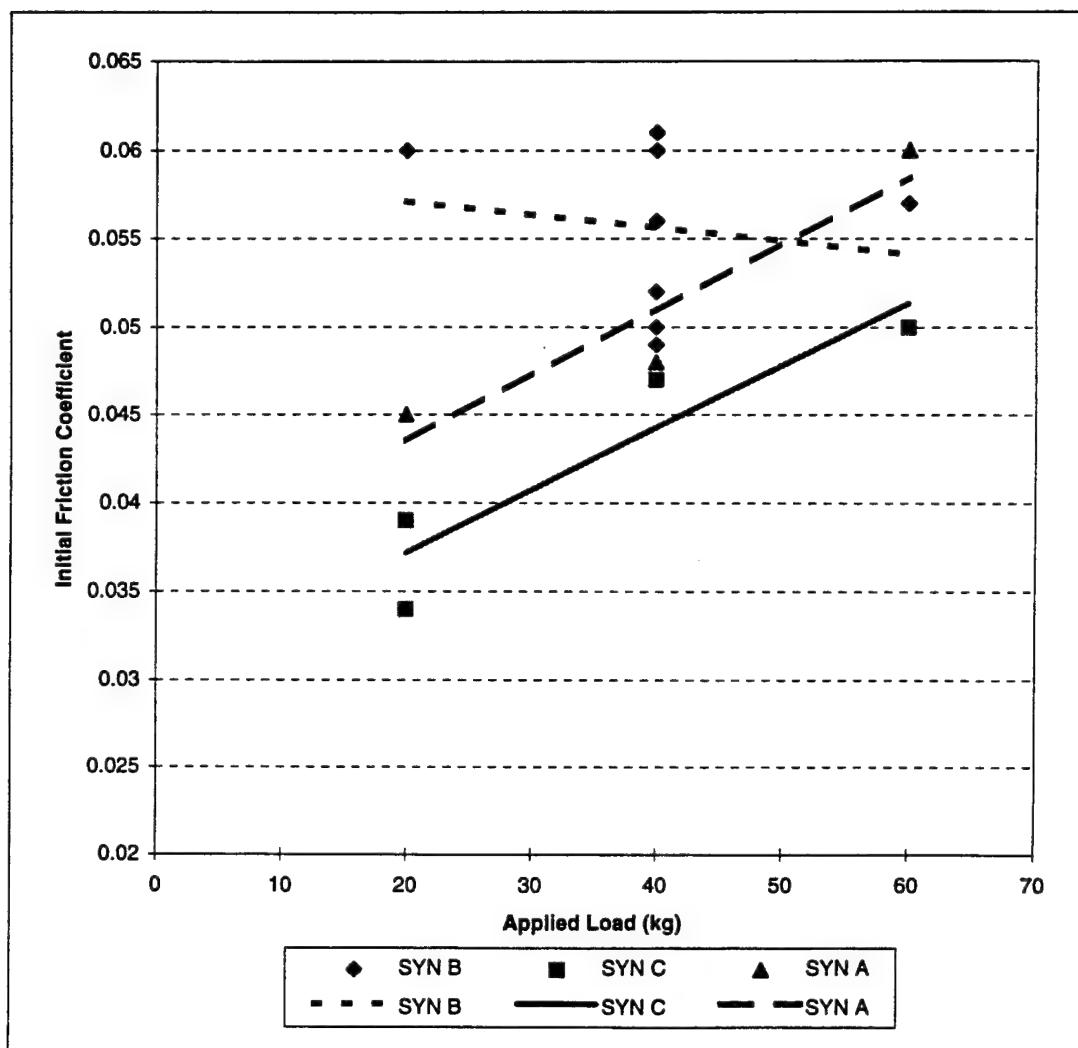
### 5.3 Grease Volatility Results

The Penn State microreactor test was used to compare the volatility of SYN A, SYN B and SYN C. The test was run for eight hours at 125 °C. These are the conditions that were found to be optimum for analyzing the oxidative properties of greases on the PSMO test [50]. Volatility is measured by percent weight loss of the grease sample after oxidation. The weight loss is due to evaporation from both the base oil and oxidized



Load: 40 kg  
Temperature: 100, 150 and 200 C  
Sliding Distance: 138 m

Figure 5.12 Initial Friction Coefficient Versus Speed



Time: 5 minutes

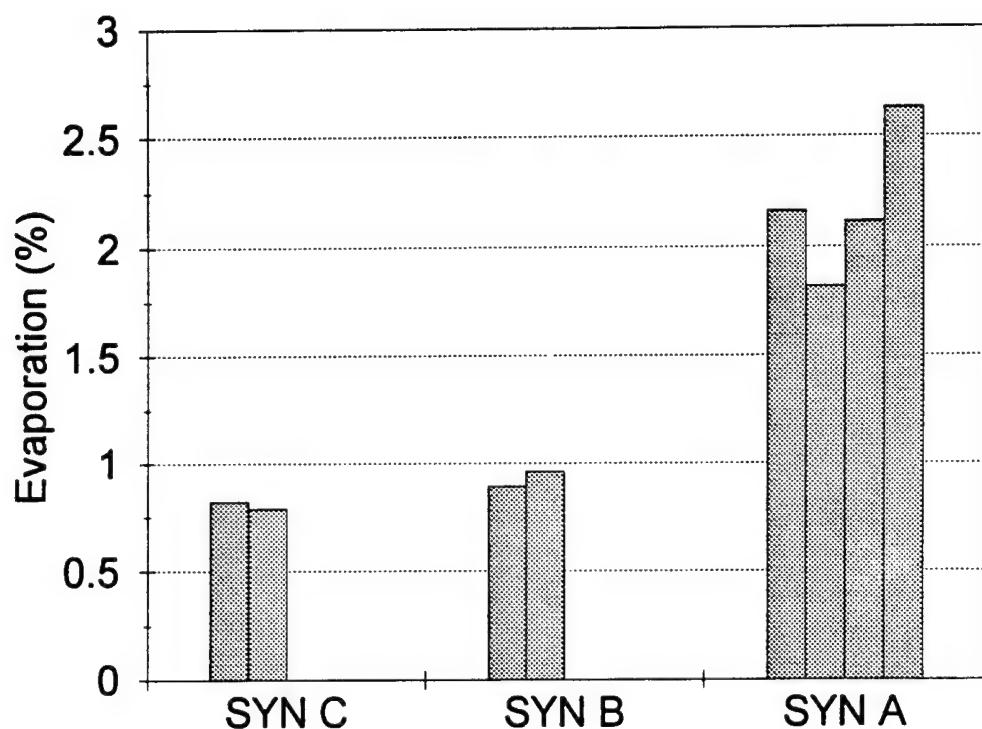
Temperature: 100 C

Speed: 1200 rpm

Figure 5.13 Initial Friction Coefficient Comparison of Synthetic Greases On Four Ball Test

reaction products. These results are presented on Figure 5.14. Both SYN B and SYN C show approximately two times less volatility loss than the current SYN A grease.

The increased stability under oxidative conditions will allow SYN B and Syn C to reduce the amount of fluid loss from the grease while in the gear system. This will help to maintain the wear protection for longer periods of time. SYN C performed slightly better than SYN B in this test due to a higher viscosity base oil. The higher viscosity oil will evaporate at a slower rate.



Temperature: 125 C  
Time: 8 hr  
Air Flow Rate: 20 cc/min

Figure 5.14 Grease PSMO Evaporation Results

## Chapter 6

### SUMMARY AND CONCLUSIONS

Development and evaluation of lubricants for use in specific marine applications have been performed. Several bench tests were used to evaluate two lubricants, a grease and an oil, in properties including: oxidation, volatility, friction, wear protection and foaming tendency. Both lubricants were compared against the current lubricant to use as a baseline.

Based on the results from the bench tests, the formulated oil that is recommended is FF PPG. FF PPG contains the polypropylene glycol PPG2 as the base oil with 0.5 weight percent DIAP, 1.0 weight percent PNA and 1.0 weight percent TBP. The approximate biodegradability of FF PPG is 48 percent compared with 20 percent for the current mineral oil.

For the grease application, a commercially available grease referred to as SYN C was recommended as the replacement. SYN C is a lithium complex soap grease with a polyalphaolefin base oil. It has an NLGI hardness ranking of 1 ½ and contains extreme pressure additives.

The first property investigated with the polyalkylene glycol fluids was foaming tendency under high shear conditions. Standard ASTM foaming methods did not duplicate the application. Therefore, a foaming test procedure was developed to duplicate

fluid performance in the system. The low molecular weight polypropylene glycols examined, including PPG2, were shown to produce no foam at concentrations above 0.4 weight percent in a water solution. The higher molecular weight polypropylene glycols were shown to produce small amounts of foam at a concentration of 4.0 weight percent. Both water soluble polyalkylene glycols, PEPG1 and PEPG2, produced foam. PPG2 did not foam in a blend with 20 weight percent PEPG2.

The wear properties of PPG2 were examined with various wear additives in a series of bench tests. The sequential four ball test was used to evaluate steel on steel contact pairs. This test is described in section 3.2. The most effective wear additives for PPG2 were found to be 5.0 weight percent TCP and 0.5 weight percent. The PPG2 with either TCP or DIAP significantly outperformed the mineral oil in this test.

The ball and three flats test was used to study a steel on nickel aluminum bronze alloy (NAB) and a steel on aluminum alloy (AL 2618 T6) contact pair. In both cases, the 0.5 weight percent of DIAP in PPG2 provided the best wear protection. TCP was found to be an ineffective antiwear additive on NAB.

A scuffing four ball test was used to evaluate the different additives ability to protect against wear at high loads. The polypropylene glycol with DIAP exhibited the best performance. The TCP was unable to protect against scuffing even at 60 kg. The current mineral oil was found to scuff at the same load as PPG2 with the DIAP. The difference was where the polypropylene glycol based lubricant showed incipient scuffing while the mineral oil showed severe scuffing.

The pins on ring test was used to study the wear behavior of NAB or Al 2618 T6

or manganese bronze on steel at temperatures of 260 °C and in a steam environment. The fully formulated polypropylene glycol lubricant, FF PPG, showed slightly improved wear protection over the current mineral oil in systems of NAB on steel and manganese bronze on steel. Lubrication of the aluminum pins proved to be a problem. FF PPG displayed higher wear rates in comparison to the mineral oil.

Oxidation stability was evaluated on the Penn State Microoxidation Test. PPG2 was found to have very little final deposit. It volatilized quickly in comparison to the current mineral oil. Increasing levels of copper antioxidant reduced the volatility, but was not utilized further due to possible environmental concerns. A 1.0 weight percent concentration of both PNA and TBP proved the best non-metal antioxidant combination.

Analysis of the greases consisted of standard wear, extreme pressure wear, friction and volatility testing. Standard wear testing was done on a four ball wear tester. The two greases exhibiting the best standard wear characteristics were SYN B and MIN A, both NLGI grade 2 greases. The softer greases SYN C and the current grease, SYN A, did not perform as well. SYN C did perform much better than SYN A overall. Extreme pressure testing was also done with a four ball machine. These results gave a ranking from best to worse of: SYN C > SYN B > MIN A > SYN A.

Extensive testing was done on the friction coefficient of SYN B and SYN C also on the four ball machine. Overall, the slightly softer SYN C was found to have a lower coefficient of friction. A general decrease in the friction coefficient was found with increasing temperatures and increasing rotating speeds. The friction coefficient was normally found to increase with increasing loads.

Volatility testing on the Penn State Microoxidation Test showed both SYN B and SYN C to have about half the volatility loss of the current SYN A. These tests were conducted at 125 °C for eight hours.

Both SYN C and SYN B proved to be effective grease replacements based on the bench test results. Pumping tests in the actual pump system found the harder SYN B grease too thick to pump efficiently through the system. For this reason, SYN C was chosen as the grease replacement.

## Chapter 7

### FUTURE WORK

Future research is needed based on the results of the aluminum pins on ring tests with the polyalkylene glycol lubricants. The black film that remains on the pins with mineral oil needs to be evaluated to determine its composition. A trial on the pins on ring tester without steam would evaluate the role of steam in this high wear being observed.

Evaluation of the oxidative products of the polyalkylene glycols should be conducted. Possibly, carboxylic acids that are formed increase the wear being observed or the acids are able to remove the black film which is likely providing wear protection.

Future work on the grease project will focus on increasing the biodegradability and overall environmental acceptability of the grease. Some of the base fluids evaluated in the oil project described here may prove as useful base oils for the grease. A variety of thickeners including clays and soaps need to be evaluated as a part of this research. Continuing research on additives will also be required.

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